U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-298 343

The First American-Soviet Symposium on Chemical Pollution of the Marine Environment Held at Odessa, USSR on May 24-28, 1977

(U.S.) Environmental Research Lab., Gulf Breeze, FL

Dec 78

United States
Environmental Protection
Agency

Environmental Research
Laboratory
Gulf Breeze FL 32561

EPA-600/9-78-038
December 1978

Research and Development

EPA

First American-Soviet Symposium on Chemical Pollution of the Marine Environment

PB 298343

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the "SPECIAL" REPORTS series. This series is reserved for reports targeted to meet the technical information needs of specific user groups. The series includes problem-oriented reports, research application reports, and executive summary documents. Examples include state-of-the-art analyses, technology assessments, design manuals, user manuals, and reports on the results of major research and development efforts.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/9-78-038

2.

3. RECIPIENT'S ACCESSION NO. PB298343

4. TITLE AND SUBTITLE
FIRST AMERICAN-SOVIET SYMPOSIUM ON CHEMICAL POLLUTION OF THE MARINE ENVIRONMENT

5. REPORT DATE December 1978

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
Karl K. Turekian, Chairman, U.S. Delegation and
Anatoliy I. Simonov, U.S.S.R. Leader, Project VI-2.1

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Environmental Research Laboratory
Gulf Breeze, FL 32561

10. PROGRAM ELEMENT NO. 1BA608

11. CONTRACT/GRANT NO. Joint U.S.-U.S.S.R. Project VI-2.1

12. SPONSORING AGENCY NAME AND ADDRESS
U.S. Environmental Protection Agency
Office of Research and Development
Environmental Research Laboratory
Gulf Breeze, Florida 32561

13. TYPE OF REPORT AND PERIOD COVERED Final, May 24-28, 1977

14. SPONSORING AGENCY CODE EPA/600/04

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This symposium, organized under a U.S.-U.S.S.R. Environmental Agreement (Project 02.06-21), focuses on the impact of chemical pollution on the world's oceans. Soviet and American specialists discuss the fate of heavy metals in estuaries and the Gulf of Mexico; transport of natural radionuclides in shelf waters of the eastern U.S.; the distribution and dynamics of trace metals in pore water and sediment; biogeochemical research on metals in the world's oceans; monitoring chemical pollution and forecasting its biological consequences; arsenic, antimony, and mercury in seawater; pollution of the Caribbean Basin; oil and oil products in surface waters of the Atlantic, Pacific, and Indian Oceans; the forms of heavy metals in seawater (e.g. mercury); methods of sampling water from the ocean surface microlayer and the technical composition of the microlayer; a method for determining mercury; scientific aspects of marine pollution problems; and the management of the quality of the marine environment. Publication of the proceedings held May 24-28, 1977, in Odessa, U.S.S.R., is in compliance with the Memorandum from the 4th Session of the Joint U.S.-U.S.S.R. Committee on Cooperation in the Field of Environmental Research.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Chemical reactions Water pollution Water resources Nuclear fuels Metal containing organic compounds Radioactive isotopes Oceanographic surveys Oil recovery Nuclides	Biogeochemical research U.S.-U.S.S.R. Agreement in the Field of Environmental Protection Fate of heavy metals Ocean surface microlayer	06/06 07/04 08/01 08/04 11/06 11/08 18/07

18. DISTRIBUTION STATEMENT
Release to public

19. SECURITY CLASS *(This Report)* Unclassified

20. SECURITY CLASS *(This page)* Unclassified

21. NO. OF PAGES 206

22. PRICE A10- A01

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

☆U.S. GOVERNMENT PRINTING OFFICE: 1979-640-004 2127 REGION NO. 4

EPA-600/9-78-038
December 1978

FIRST AMERICAN-SOVIET SYMPOSIUM ON CHEMICAL POLLUTION OF THE MARINE ENVIRONMENT

Odessa, USSR

May 24 to 28, 1977

Symposium Sponsored as Part of the U.S.-U.S.S.R.
Agreement on Protection of the Environment

Compiled by

Karl K. Turekian
Chairman, U.S. Delegation

and

Anatoliy I. Simonov
U.S.S.R. Leader, Project VI-2.1

ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
GULF BREEZE, FLORIDA 32561

ia

DISCLAIMER

This report has been reviewed by the Gulf Breeze Environmental Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWORD

The Joint American-Soviet Committee on Cooperation in the Field of Environmental Protection, established by an agreement signed May 23, 1972, in Moscow, identified 11 ecological problem areas for cooperative investigation and exchange of information. In accordance with these objectives, the First American-Soviet Symposium on Chemical Pollution of the Marine Environment was convened May 24-28, 1977, in Odessa, U.S.S.R., for a joint examination of the accumulation and spread of chemical pollution in international oceanic waters.

In this publication, the proceedings are arranged in the order of their presentation. Discussions engendered by papers presented in English and Russian reflected interest of participants in reconvening a Second U.S.-U.S.S.R. Symposium on Chemical Pollution in the U.S. within two or three years. Suggested topics for the subsequent session were: transformation and fate of chemical pollutants in the marine environment; influence of pollution on physical and chemical professes; and methods for determining pollution in the marine environment.

Success of the symposium resulted from the combined efforts of planners, travel coordinators, speakers, and translators. Publication of the proceedings by the Environmental Research Laboratory, U. S. Environmental Protection Agency (EPA), Gulf Breeze, Florida, fulfills the protocol agreement for Project VI-2.1 requiring simultaneous and independent publication in both countries after coordination of manuscripts.

Thomas W. Duke

Thomas W. Duke
Director
Environmental Research Laboratory
Gulf Breeze, Florida
U. S. Leader of Project VI-2.1

ABSTRACT

The First American-Soviet Symposium on Chemical Pollution of the Marine Environment examines the impact of chemical pollutants on the world's oceans and estuaries. Subjects of the papers presented by American and Soviet specialists include: fate of heavy metals in estuaries and the Gulf of Mexico; transport of natural radionuclides in shelf waters of the eastern U.S.; the distribution and dynamics of trace metals in pore water and sediments; biogeochemical research on metals in the world's oceans; monitoring chemical pollution and forecasting its biological consequences; arsenic, antimony, and mercury in seawater; pollution of the Caribbean Basin; oil and oil products in surface waters of the Atlantic, Pacific, and Indian Oceans; the forms of heavy metals in seawater (e.g. mercury); methods of sampling water from the ocean surface microlayer and the technical composition of the microlayer; a method for determining mercury; scientific aspects of marine pollution problems; and the management of the quality of the marine environment. Publication of the proceedings held May 24-28, 1977, in Odessa, U.S.S.R., is in compliance with the Memorandum from the 4th Session of the Joint U.S.-U.S.S.R. Committee on Cooperation in the Field of Environmental Research.

CONTENTS

Foreword iii
Abstract iv

Introduction 1

Protocol 3

Participants in the Symposium 5

Biological Investigations of Metals in the World's Oceans in Connection with Monitoring of the Chemical Pollution of the Marine Environment, N. P. Morozov, S. A. Patin, and C. A. Petukhov 8

Effect on the Diagenetic Status of Sediments on Trace Metal in Pore Waters, Michael L. Bender 18

The Fate of Metals in Estuaries, Karl K. Turekian 27

The Structure of Arsenic and Stibium Fields in the Caribbean Sea, A. I. Ryabinin and A. S. Romanov 39

Chemical Forms of Mercury in Marine Waters, A. K. Prokof'yev. 47

The Fate of Heavy Metals Added to the Gulf of Mexico by the Mississippi River, B. J. Presley 61

Oil Products in Surface Waters of the Pacific and Indian Oceans, M. Nesterova, I. A. Nemirovskaya, N. Anufrieva, and V. Maslov . . 76

Oil Pollution Studies in the Norwegian and the Greenland Seas, V. M. Smagin and V. S. Rachkov 84

Study of Methods of Sampling Seawater from the Ocean's Surface Microlayer and Results of Determination of Oil in Various Regions of the Atlantic Ocean, V.I. Mikhaylov and S.G. Oradovskiy. 92

Cesium-137 as a Tracer for Reactive Pollutants in Estuarine Sediments, H. J. Simpson, C. R. Olsen, R. Bopp, P. M. Bower, R. M. Trier, and S. C. Williams 102

The Distribution of Pollutants in the Caribbean Basin, M. M. Domanov, B. A. Nelepo, and V. N. Stepanov 114

Suspended Particulate Matter and Natural Radionuclides as Tracers of Pollutant Transports in Continental Shelf Waters of the Eastern U. S., Pierre E. Biscaye, Curtis R. Olsen, and Guy Mathieu 125

Trace Element Geochemistry of Continental Shelf Waters of the Southeastern United States, Herbert L. Windom 148

The Flameless Atomic Absorption Method for Mercury Determination and Its Use in Controlling Environmental Pollution, N. S. Poleuktov and Yu. U. Zelyukova 159

The Scientific Principles of the Problem of Seawater Pollution, A. I. Simonov and A. N. Zubakina 164

Monitoring of Marine Environment as an Information Basis for Economic-ecological Control, M. T. Meleshkin, A. I. Simonov, A. M. Bronfman, V. E. Glushkov, and A. L. Suvorovsky 183

Appendix

Protocol of the Working Meeting of Soviet and American Specialists . . 198

INTRODUCTION

Karl K. Turekian
Chairman, U.S. Delegation

There are a number of ways of trying to assess the impact of man's activities on living marine organisms. One direct method is to measure the direct biological effects in the form of mortalities, inhibitions to activity, and actual extinction of species. However, many effects can have less acute influences that are nevertheless important over a long-time scale. Therefore, the application of direct methods can be insufficient for studying the effects of chemical pollution on the living marine environment. Various chemical, biological, and physical methods for evaluating the state of the living and non-living marine environment are used in research on this problem.

In order to assess changes in the "health" of the sea under the influence of chemical pollution, we must know how it accommodates perturbations under normal conditions. Only then can we try to assess the levels of acceptable insults for which the natural assimilation processes will overcome the processes that pollute the world's oceans, and predict the dynamics of the levels of pollution.

U.S. and Soviet specialists working under the joint project "Effect of Pollutants on Marine Organisms" approached the Symposium on Chemical Pollution of the Marine Environment with an understanding of the scientific aspects of pollution problems. The Symposium was held in Odessa USSR from May 24-28, 1977, and was organized in accordance with the Memorandum from the Fifth Session of the Joint U.S.-U.S.S.R. Committee on Cooperation in the Field of Environmental Protection.

The fluxes of metals, radionuclides, particulate material, and organochlorine pesticides and hydrocarbons in estuarine systems are sufficiently intense to require our special attention. These systems represent a region of the sea heavily used by man in all his activities. Papers presented by the U.S. members of the joint seminar concentrated primarily on problems of the coastal and estuarine zone.

The papers presented by the Soviet specialists were concerned with a discussion of problems associated with pollution in the open ocean, focusing primarily on organic (mainly hydrocarbon) impacts. This approach demonstrates the global character of chemical pollution of the oceans.

In this manner, the Soviet and American papers complement each other in attempts to reveal the whole picture of pollution in the world's oceans.

These two directions guaranteed the fruitful work of the Symposium and opened the possibility of future collaborations. The members of the U.S. delegation were pleased with the opportunity to conduct valuable discussions with their Soviet counterparts.

PROTOCOL

OF THE FIRST U.S.-U.S.S.R. SYMPOSIUM
ON
CHEMICAL POLLUTION OF THE MARINE ENVIRONMENT

In accordance with the principles laid down in the protocol from the Working Group Meeting held in the U.S.S.R. in July 1976 and the Memorandum of Implementation from the Fifth Meeting of the U.S.-U.S.S.R. Joint Committee on Cooperation in the Field of Environmental Protection, a Joint U.S.-U.S.S.R. Symposium on Chemical Pollution of the Marine Environment was held in Odessa, U.S.S.R. from May 24 through 28, 1977.

The Symposium was co-chaired by Dr. Karl K. Turekian, Professor of Geology and Geophysics at Yale University (U.S.) and Professor Anthony I. Simonov, Division Director, State Oceanographic Institute (U.S.S.R.). A list of participants is attached.

The participants in the symposium presented papers on tracers of pollutants in estuarine sediments and U.S. continental shelf waters; the fate of heavy metals in estuaries and the Gulf of Mexico; transport of natural radionuclides in shelf waters of the eastern U.S.; the distribution and dynamics of trace metals in pore water and sediments; biogeochemical research on metals in the world ocean; monitoring chemical pollution and forecasting its biological consequences; arsenic, antimony and mercury in seawater; pollution of the Caribbean Basin; oil and oil products in surface waters of the Atlantic, Pacific and Indian Oceans; the forms of heavy metals in seawater (e.g. mercury); methods of sampling water from the ocean surface microlayer and the technical composition of the microlayer; a method for determining mercury; scientific aspects of marine pollution problems; and the management of the quality of the marine environment.

Stimulating discussions were held after each presentation. The participants in the symposium expressed the desire to conduct a Second U.S.-U.S.S.R. Symposium on Chemical Pollution of the Marine Environment in two to three years in the U.S. The following possible topics for this symposium were mentioned; transformation, fate of pollutants (oil and oil products, heavy metals et al.) in the marine environment, in sediments, and in the surface microlayer; influence of pollution on physical and chemical processes; input of pollutants from rivers to coastal and oceanic waters; fate and transport of radionuclides; and methods for determining pollution in the marine environment.

During the visit of the American delegation to the U.S.S.R., the American scientists visited the Institute of Economics of the Ukrainian Academy of

Sciences, the R/V *Victor Bugayev* of the State Oceanographic Institute in Odessa, and the Arctic and Antarctic Institute and its research vessel the *Professor Zubov* in Leningrad.

The Symposium was held in an atmosphere of friendly cooperation and has been of mutual benefit to both sides. The U.S. specialists wish to express their gratitude to the Soviet delegation for such a well organized symposium and for the gracious hospitality shown them during their visit. They also wish to thank the interpreters for their excellent services.

This protocol was signed in Odessa on May 28, 1977, in two copies, Russian and English, both copies being equally valid.

K. Turekian

U.S. Chairman

A. Simonov

U.S.S.R. Chairman

PARTICIPANTS

AMERICAN SIDE

Dr. Thomas W. Duke
Director, Environmental Research Laboratory
U.S. Environmental Protection Agency
Gulf Breeze, Florida 32561

Dr. Karl K. Turekian
Co-chairman of the Symposium
Professor of Geology and Geophysics
Department of Geology and Geophysics
Yale University
New Haven, Connecticut 06520

Dr. Michael L. Bender
Assistant Professor of Oceanography
Graduate School of Oceanography
University of Rhode Island
Kingston, Rhode Island 02881

Dr. H. James Simpson
Assistant Professor of Geological Sciences
Lamont-Doherty Geological Observatory
Palisades, New York 10964

Dr. Pierre E. Biscaye
Senior Research Associate
Lamont-Doherty Geological Observatory
Palisades, New York 10964

Dr. B. J. Presley
Associate Professor
Department of Oceanography
Texas A & M University
College Station, Texas 77843

Dr. Herbert L. Windom
Associate Professor
Skidaway Institute of Oceanography
University System of Georgia
P. O. Box 13687
Savannah, Georgia 31406

Dr. Richard Hittinger
Research Specialist
Graduate School of Oceanography
University of Rhode Island
Narragansett, Rhode Island 02882

Ms. Elaine M. Fitzback
Soviet Project Coordinator
Gulf Breeze Environmental Research Laboratory
Environmental Protection Agency
Gulf Breeze, Florida 32561

SOVIET SIDE

A. I. Simonov
Co-chairman of the Symposium
State Oceanographic Institute
Moscow

M. P. Nesterova
Deputy Co-chairman
P.P. Shershov Oceanology Institute, U.S.S.R. Academy of Sciences

Ye. A. Sobchenko
Director of the Odessa Branch of the State Oceanographic Institute
Odessa

M. T. Meleshkin
Economics Institute of the Ukrainian Academy of Sciences
Odessa

A. K. Prokof'yev
State Oceanographic Institute
Moscow

A. I. Bronfman
Economics Institute of the Ukrainian Academy of Sciences
Odessa

M. M. Domanov
P.P. Shershov Oceanology Institute, U.S.S.R. Academy of Sciences
Moscow

A. I. Zubakina
State Oceanographic Institute
Moscow

V. I. Mikhailov
State Oceanographic Institute
Odessa Branch

N. P. Morozov
P.P. Shershov Oceanology Institute, U.S.S.R. Academy of Sciences

I. A. Nemirovskaya
P.P. Shershov Oceanology Institute, U.S.S.R. Academy of Sciences
Moscow

S. G. Oradovskiy
State Oceanographic Institute
Moscow

S. A. Patin
All-Union Fisheries and Oceanography Scientific Research Institute
Moscow

V. M. Smagin
Arctic and Antarctic Research Institute, Leningrad

Yu. V. Zelyukova
Physical-Chemical Institute of the Ukranian S.S.R. Academy of Sciences

V. Ye. Glushkov
Economics Institute of the Ukrainian Academy of Sciences
Odessa

A. L. Suvorovsky
Economics Institute of the Ukrainian Academy of Sciences
Odessa

M. K. Viktorova
Interpreter

S. M. Sheyman
Interpreter

BIOLOGICAL INVESTIGATIONS OF METALS IN THE WORLD'S OCEANS IN CONNECTION WITH MONITORING THE MARINE ENVIRONMENT

N. P. Morozov, S. A. Patin, and S. A. Petukhov
P.P. Shershov Oceanology Institute, U.S.S.R. Academy of Sciences

It is well-known that heavy and transitional metals, such as components of the pollution of marine ecosystems, are subjected to man-made disturbances affecting their concentrations and relationships in the environment of hydrobionts. These disturbances affect the natural content of corresponding trace elements (for example, iron, manganese, zinc, and copper), many of which are very important for the vital activity of hydrobionts. Therefore, monitoring of marine pollution by metals and the interpretation of results are impossible without analyses and generalization of data concerned with natural (background) levels of metal content in biotic and abiotic components in marine ecosystems.

In this report, we attempt to solve this problem on the basis of biochemical data obtained in laboratories of radiative and chemical ecology of the All-Union Scientific Research Institute of Marine Fishery and Oceanography.

Methods of sampling and preliminary treatment of water samples, particulate, plankton, benthos, nectone, and bottom sediments were similar to generally accepted procedures. Analyses were made by spectrophotometry with spectrophotometer Hitachi-207 and mercury analyzer Coleman MAS-50, according to procedures described earlier (5, 6, 12). The coefficient for the variation of results of parallel counts was 10 to 20 per cent for different ecosystems.

Summarized results of the determination of 10 metals in samples of water, particulate, and hydrobionts from different parts of the world's oceans are presented in Tables 1 to 3 and in Fig. 1. The combination of data shows a general picture of modern content and distribution of trace elements of the metal group in marine and oceanic ecosystems. On the whole, our data agree with published data (1, 2, 11, 14, 15, 16, 17). However, there are some understandable discrepancies in methods, sampling, treatment, and analyses of samples, as well as natural variation of metalic concentrations due to geographical, seasonal, and other factors.

For the North Atlantic, we showed that the spatial distribution of metals in question is connected with the current system of the region (7). Data on the Sea of Azov show that intensive summer bioproduction in shallow water may lead to a notable decrease of a number of metals in water depth, due to biosedimentation to the bottom. For this reason, relatively low concentrations

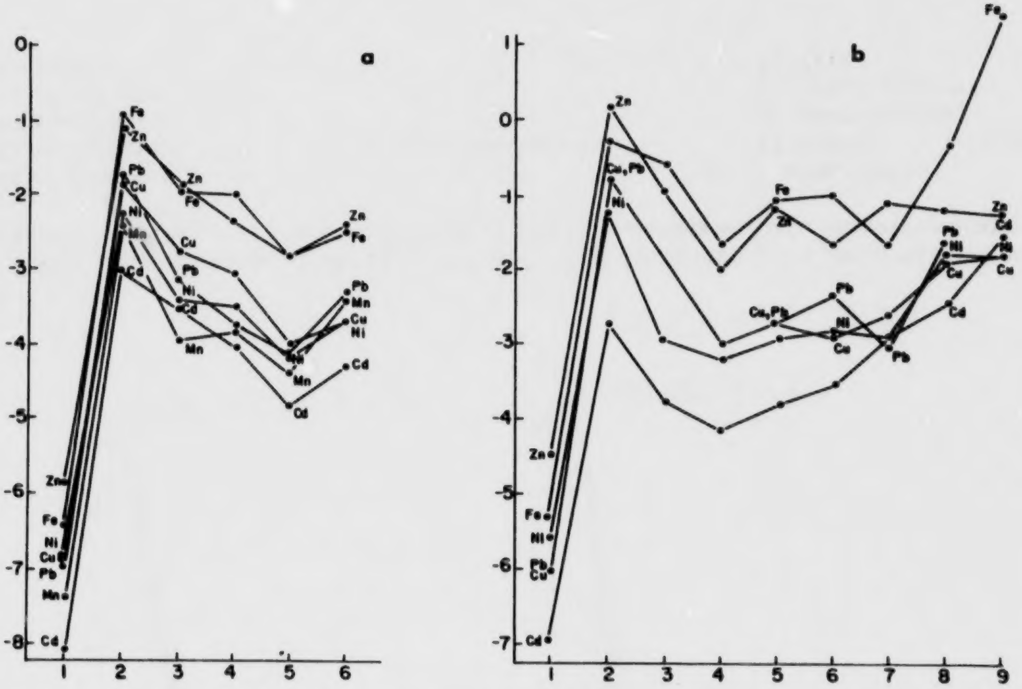


Figure 1. Mean metal concentration distributions with main components of some marine and fresh water ecosystems (ordinate--logarithms of mean metal concentrations; absciss--ecosystem components).

a. pelagium of the ocean:
1) marine waters;
2) particulate;
3) phytoplankton;
4) zooplankton;
5) fish (muscles);
6) fish (skeleton).

b. Sea of Japan:
1) marine waters;
2) particulate;
3) total plankton;
4) fish (muscles);
5) fish (skin);
6) phytobenthos;
7) zoobenthos (soft tissues);
8) zoobenthos (hard structures);
9) bottom sediments.

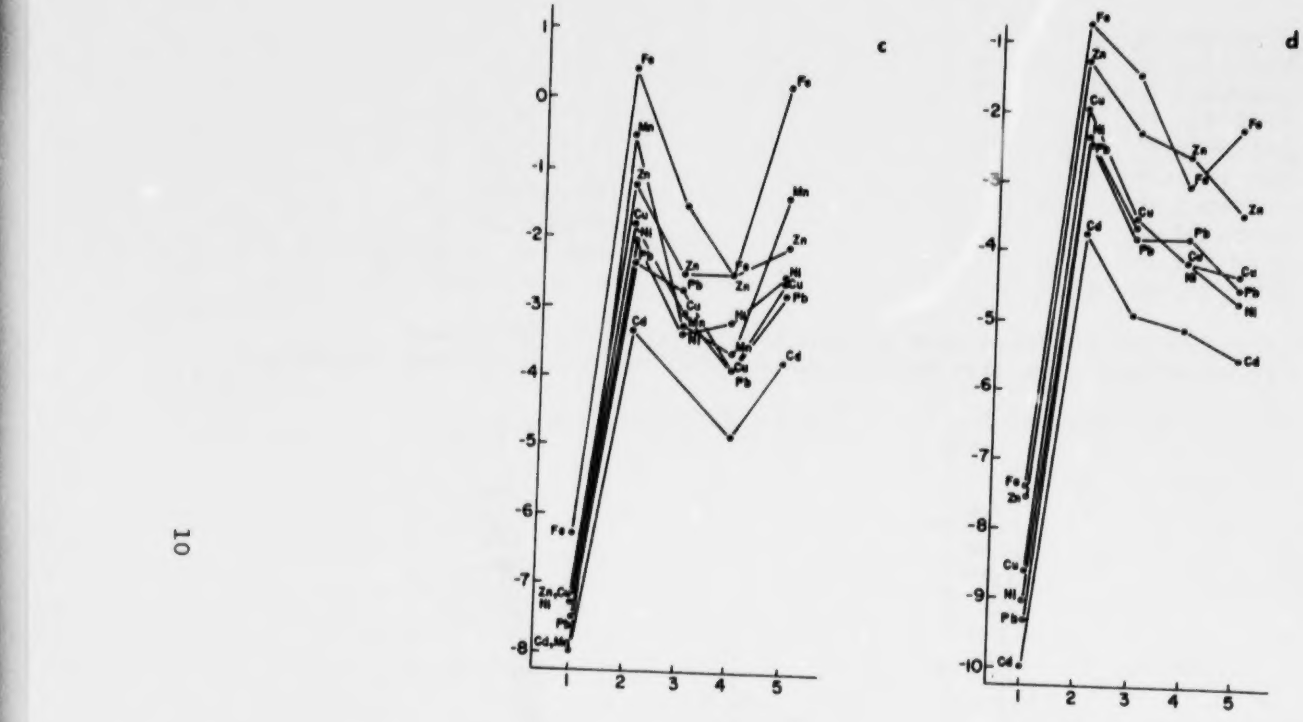


Figure 1. Mean metal concentration distributions with main components of some marine and fresh water ecosystems (ordinate--logarithms of mean metal concentrations; absciss--ecosystem components).

c. Sea of Azov:
1) marine water; 5) bottom sediments
2) particulate;
3) total plankton;
4) fish;

d. Khasan Lake:
1) water; 5) phytobenthos.
2) particulate;
3) total plankton
4) fish;

of zinc, copper, and nickel are found in Sea of Azov (Table 1), where seasonal variations of trace element contents are possible.

Table 1 shows that the general order of magnitude and general sequence of various metal concentrations in surface waters of different regions, with salinity from 35 per cent (oceanic pelagium) to higher percentages (freshened seas) are similar. These data also show a trend of the increased concentrations of the majority of metals in both water and particulate at the transition from the oceanic pelagium to neritic zone and internal seas. This trend follows a general geochemical regularity of the increase of the effect of terrigenic freshwater run-off on chemical composition of marine water bodies. At the same time, in accordance with published data (8, 9), a similar trend is characteristic of a large-scale distribution of technogenic pollutants (metals included) in the world's oceans. The problem of the role and relationship of these factors in the formation of marine elements should result from chemical monitoring, providing for each region's peculiarity.

The data in Table 2 are concerned with the content of heavy and transitional metals in plankton biomass. They reflect rather high variability of average concentrations undoubtedly connected with a diversity of the composition of plankton communities studied, and the process of bioaccumulation of individual trace elements in phyto- and zooplankton organisms. Another peculiarity of trace element composition lies in the predominance of elevated concentrations of metals in plankton of neritic and fresh water, compared to oceanic pelagic populations. A similar trend was mentioned above for surface waters. Finally, the last reason for a general conjunction of marine water composition and plankton bionts lies in the fact that, in majority of cases, one and the same sequence of decreasing concentration is followed in the series iron-zinc-copper.

In general, the above is true for the ichthyofauna, although not to the same extent as for plankton. Data presented in Table 3 illustrate typical levels of metal contents in muscles and skeletons of commercial fish of the world's oceans and fresh water.

A general picture of heavy metal concentration distribution in abiotic and biotic components of various marine ecosystems, oceanic pelagrium, and Seas of Japan and Azov is given in Fig. 1 (data on Khasan Lake are also presented for comparison). First, we note a similar variation of curves: the largest concentrations of each of the metals are observed in particulate and bottom sediments, then comes plankton, benthos, and fish. The greatest accumulating capacity of particulate is connected with its higher dispersity and the intensity of sorbing processes at the boundary of interface with water medium. The physico-chemical nature of metal absorption is indicated in this case by the fact that the particulate retains a typical relationship for the marine water metal and their sequence in the series of concentrations. This fact is indicated by a parallelism of lines combining mean metal concentrations in water and particulate.

These data suggest that the trace element composition of ecological groups of biotic population of marine regions generally reflects the content and distribution of trace elements in nonliving components of ecosystems.

Reproduced from best available copy.

TABLE 1. CONTENT OF HEAVY AND TRANSITIONAL METALS IN SURFACE WATER AND PARTICULATE

	Quantity of samples	Iron		Manganese		Zinc		Copper		Nickel		Cobalt		Chromium		Lead		Cadmium		Mercury		Reference
		solv. mg/l	partic mg %	solv. mg/l	part. mg %	solv mg/l	pat. mg %	solv. mg/l	part. mg %	solv. mg/l	part. mg %	solv. mg/l	part mg %	solv. mg/l	part. mg %	solv. mg/l	part. mg %	solv. mg/l	part. mg %	solv. mg/l	part. mg %	
Atlantic ocean (Northern part)	80	3.0	0.27/0.04	0.4	0.03/0.003	9.0	0.64/0.084	1.0	0.09/0.014	2.0	0.09/0.005	0.3				0.9	0.12/0.017	0.2		0.07		Given work
Pacific ocean	27															0.25		0.11		0.16		—"—
Indian ocean	8	5.6	0.19	0.3	0.004	19.9	0.07	1.7	0.013	1.7	0.006	0.2				0.21	0.007	0.13	0.0007			—"—
Mean		4.3	0.12	0.4	8/0.004	14.5	0.077	1.4	0.014	1.9	0.006	0.3				0.45	0.012	0.15	0.001	0.12		—"—
Mean for oceanic water		5.0		0.3		3.0		2.0		2.0		0.05		0.5		0.02		0.08		0.1		Goldberg, 1972
Sea of Japan	15*	5.0	26.3/0.33		0.4/0.004	34.2	6.6/0.151	1.0	0.9/0.016	1.1	0.4/0.006	0.2				1.4	0.4/0.017	0.1	0.05/0.0002	0.8		Given work
Bay of Peter the Great	3	6.5	47.3/0.48		3.4/0.016	56.5	9.2/0.055	1.0	9.6/0.028	1.0	1.0/0.005	0.3				0.5	0.6/0.013	0.1	0.07/0.0006	0.6		—"—
North Sea	35	11.0				26.0		2.7		2.2		0.3				1.0				0.3		—"—
Black Sea	66	7.0	1.0/0.05	0.5	0.4/0.015	20.0	3.5/0.25	4.0	0.9/0.03	2.0	0.3/0.01	0.5				3.0	0.08/0.015	1.5				—"—
the Baltic Sea	11	4.4	7.39/0.39	0.7	0.75/0.08	11.0	1.48/0.10	3.2	0.41/0.032	0.3	0.12/0.012	0.3	0.02/0.002		0.03/0.002	1.4	0.16/0.013	0.2	0.007/0.006	0.14		—"—
Bay of Riga	6	5.5	27.6/1.21	0.5	2.53/0.15	15.7	3.81/0.14	3.6	0.79/0.031	0.2	0.25/0.010	0.5	0.07/0.005		0.30/0.003	1.5	0.45/0.014	0.3	0.003/0.001	0.17		—"—
Mediterranean Sea	20	5.2	0.6/0.13	0.3	0.05/0.008	9.0	0.31/0.046	1.1	0.06/0.005	1.4	0.07/0.008	0.4			"	1.0	0.08/0.01	0.2		0.1		—"—
Sea of Azov	6	5.4	37.18/2.76	0.1	6.11/0.34	0.5	1.43/0.085	0.5	0.35/0.016	0.5	0.17/0.010	0.3	0.07/0.005		0.25/0.001	3.0	0.09/0.005	1.5	0.005/0.0005			—"—
Mean for marine water		6.5	8.82/0.33	1.5	0.25/0.027	20.0	2.97/0.14	2.4	0.29/0.021	1.4	0.08/0.008	0.38	0.08/0.002		0.02/0.003	1.54	0.16/0.014	0.5	0.019/0.0034	0.39		—"—
Mean for fresh water**		670	[illegible]/5.0	7.0	[illegible]/0.238	20.0	[illegible]/0.148	7.0	19.4/0.008	0.3	18.1/0.009	0.1	5.2/0.0016	1.0		3.0	[illegible]/0.004			0.08		Goldberg et al 1972

* - While calculating mean values for metal content in marine water data for Sea of Azov were not taken into account.

** - Mean content of metals in river water particulates (mg/l and per cent) were estimated from data of G.S.Konovalov, et al. (1966 a,b) for 16 largest rivers of the USSR.

TABLE 2. TRANSITIONAL AND HEAVY METAL CONTENTS IN PLANKTON OF OCEANIC, MARINE, AND FRESH WATER (mg/kg raw mass)

Region	Sample charact.	Fe	Mn	Zn	Cu	Ni	Co	Cr	Pb	Cd
Atlantic Ocean (Southern part)	phyto-	7.2	0.31	19.0	5.8	6.05			1.28	
	zoo-	63.6	1.15	44.9	3.5	2.5			8.85	
Indian Ocean	phyto-	214.1	1.9	249.0	29.3	2.4	0.5	2.8	14.0	0.28
	zoo-	137.0	1.8	48.0	13.6	2.7	0.5	2.0	1.4	0.12
Mean for oceanic plankton	phyto-	110.0	1.1	134	17.6	4.2	0.5	2.8	7.6	0.3
	zoo-	100.0	1.5	47	8.6	2.6	0.5	2.0	5.1	0.1
Sea of Japan	total	55.5	0.9	97.9	5.5	1.8	0.3	1.7	11.6	0.32
Bay of Peter the Great	total	226.2	0.9	110.5	12.1	1.2	0.16	11.6	13.7	0.17
Khasan Lake	total	378	19.8	48.1	31.5	2.3	0.17	2.25	1.75	0.13

TABLE 3. CONTENT OF TRANSITIONAL AND HEAVY METALS IN ICHTHIOFAUNA OF OCEANIC, MARINE, AND FRESH WATER (mg/kg raw mass)

	Tissue	Quant. of Samples	Fe	Mn	Zn	Cu	Ni	Co	Cr	Pb	Cd	Hg
Oceanic	muscles	50	14.4	0.4	14.8	0.9	0.7	0.2	0.3	0.6	0.14	0.07
	skeleton	50	30.4	3.7	38.5	2.1	2.1	1.1	4.2	4.8	0.48	0.05
Marine and Semitransitional	muscles	41	32.1	1.8	37.3	1.2	2.3	0.4	0.9	2.0	0.10	0.14
	skeleton	41	121.9	9.6	74.2	2.7	8.1	1.2	4.3	4.4	0.48	
Fresh water	muscles	24	51.0	2.0	59.8	1.0	1.2	0.2	0.5	0.9	0.10	
	skeleton	24	105.8	12.1	130.4	2.4	3.2	1.2	3.1	5.4	0.46	

This conclusion conforms with a general picture of chemical element distribution in the marine biosphere (9). Almost always one finds in every area that zinc and iron dominate among metals studied, while cobalt and cadmium are present in minimum quantities.

The greatest variability of metal content is characteristic of bottom fauna, which includes almost all species selectively concentrating chemical elements. This variability may be connected with both diversity of chemical composition of a biotope of benthos populations and peculiarities of their mode of life (presence of sedentary forms), feeding habits (filtration mechanism), and metabolism.

The data presented allow us to arrive at some conclusions and recommendations in connection with monitoring sea and ocean pollution by metals:

1. The system of observations of the content and dynamics of trace metals in seas should be of a complex character and cover basic components of the ecosystem, determining biogeochemical cycles in epipelagium of the ocean (water, particulate, and plankton) and neritic zone (water, particulate, plankton, and benthos).

2. In regions with large biomass and productivity (internal shallow seas in particular), it is reasonable to combine chemical monitoring with simultaneous observations of the primary production, biomass, and species structure of plankton communities.

3. Biological indications of anthropogenic disturbance of trace element composition of the marine environment are mostly possible through analyzing results of tests with benthos organisms that often come into contact with concentrators of metals. Seston (particularly its nonliving component) reflects the general variations (sequences) of concentrations and their relationship in seawater.

4. Efforts in the field of monitoring metals in the world's oceans should focus on the neritic zone and internal seas, where biogeochemical regional anomalies of anthropogenic characteristics are possible. Oceanic pelagium data should be interpreted as background on natural characteristics of metal content in the marine biosphere.

REFERENCES

1. Vinogradov, A.P. 1967. Introduction to Ocean Geochemistry. Nauka, Moscow, p. 212.

2. Isibasi, M. 1968. Principles of Quantitative Distribution of Chemical Elements in Seawater, including So-called Nutrient Elements. In: Osnovnye Problemy Okeanologii (Basic Problems of Oceanology), Nauka, Moscow, pp. 97-108.

3. Konovalov, G.S., A.A. Ivanova, and T. Kh. Kolesnikova. 1966. Microelements in Water and Suspended Particles of the USSR Asiatic Territory Rivers. Gidrokhimi-cheskiye Materialy (Geochemical Materials), Vol XII, Leningrad, pp. 112-123.

4. Konovalov, G.S., A.A. Ivanova, and T. Kh. Kolesnikova. 1966. Rare and Dispersed Elements (Microelements) in Water and Suspended Particles of the USSR European Territory Rivers. Gidrokhimicheskiye Materialy, Vol. XII, Leningrad, pp. 94-111.

5. Morozov, N.P.,and L.L. Demina. 1944. Extraction and Atomic Absorption Spectrophotometric Methods Application Used to Determine Heavy Metals in Seawater. Proceedings of VNIRO. Vol. 100, pp. 23-27.

6. Morozov, N.P., A.A. Tikhomirova, and Ye. M. Nikonenko. 1974. Determining the Microelement Composition of Marine Organisms. Proceedings of VNIRO, Vol. 100,pp. 28-31.

7. Morozov, N.P., S.A. Patin, and L.L. Demina. 1975. Transitional and Heavy Metals in North Atlantic Waters. Proceedings GOIN, Vol. 127, pp. 77-94.

8. Patin, S.A. 1971. Pollution of the World's Oceans. Rybnoye Khozyaistvo (Fishing Industry), No. 5, pp. 5-7.

9. Patin, S.A. 1973. Several Characteristics of the Metal Distribution in the Ocean's Pelagic Ecosystem. Okeonologiya, Vol XIII, Issue 2, pp. 255-258.

10. Patin, S.A. and N.P. Morozov. 1974. Several Aspects of Marine Pollution by Heavy Metals. Proceedings of VNIRO, Vol. 100, pp. 7-12.

11. Saukov, A.A., N. Kh. Aidinyan, and N.A. Ozerova. 1972. Synopsis of the Geochemistry of Mercury. Nauka, Moscow, p. 335.

12. Tikhomirova, A.A., S.A. Patin, and N.P. Morozov. 1976. Joint Concentration and Determination of Mercury, Lead, and Cadmium in Seawater. Zhurnal Analiticheskoi Khimii (Journal of Analytical Chemistry). Vol. XXXI, 2, pp. 282-285.

13. Goldberg, E.D. 1972. Baseline Studies of Pollutants in the Marine Environment and Research Recommendations. The IDOE Baseline Conference, May 24-26, 1972, New York.

14. Goldberg, E.D., W.S. Broecker, M.G. Gross, and K.K. Turekian. 1972. Marine Chemistry. Radioactivity in the Marine Environment. National Academy of Sciences, Washington, D.C.

15. Spencer, D.W. and P.G. Brewer. 1969. The Distribution of Copper, Zinc, and Nickel in Seawater of the Gulf of Mexico and Sargasso Sea. Geochim. et. Cosmochim. Acta, Vol. 33, No. 3.

16. Szabo, B.J. 1968. Trace Elements Content of Plankton Population from the Bahamas. Caribb. J. Sci., Vol. 8, No. 3-4.

17. Wolfe, D.A., and T.R. Rice. 1966. Nutrient Elements in Seawater. Environ. Biol., No. 7.

EFFECT ON THE DIAGENETIC STATUS OF SEDIMENTS ON THE CONCENTRATIONS OF TRACE METAL IN PORE WATERS

Michael L. Bender
Gary P. Klinkhammer
Graduate School of Oceanography
University of Rhode Island
Kingston, RI 02881

ABSTRACT

As oxidation of organic matter in sediments proceeds, dissolved interstitial oxygen, nitrate, and $SO_4^=$ are reduced in that order. In oxygen-bearing pore waters, the manganese and iron concentrations are very low due to the formation of insoluble oxidized compounds. When oxygen is depleted, manganese and iron concentrations rise. In sulfate-reducing sediments, interstitial Cu, Cd, and Ni concentrations are equal to or less than values in bottom waters, presumably due to formation of insoluble sulfides.

Rates of release of metals to bottom waters ("benthic fluxes") have been studied by direct measurement in the northeastern United States (Narragansett Bay). In an area where diagenesis was proceeding by sulfate reduction and a high interstitial manganese concentration was very close to the sediment-water interface, the manganese benthic flux was found to be great enough so that diffusion from sediments was clearly an important source to the overlying waters. Estimated upper limits for benthic fluxes of copper, nickel, and cadmium indicated that release from sediments was not important in the balance of these metals in the overlying waters.

Trace metals may be released to the water column from metal-rich wastes dumped in the nearshore environment. The rate at which metals are released will depend on their concentrations in pore waters. Pore-water concentrations, in turn, are controlled in part by diagenetic reactions in the sediments. The sequence of these reactions, predicted according to decreasing release of energy per mole of organic carbon oxidized, is as follows:

$$\text{(1)}\quad 5(CH_2O)_{106}\,(NH_3)_{16}\,(H_3PO_4) + 690\ O_2 \rightarrow 530\ CO_2 + 80\ HNO_3 + 5H_3PO_4 + 610\ H_2O$$

$$\text{(2)}\quad 5(CH_2O)_{106}\,(NH_3)_{16}\,(H_3PO_4) + 472\ HNO_2 \rightarrow 530\ CO_2 + 276\ N_2 + 886\ H_2O + 5\ H_3PO_4$$

$$\text{(3)}\quad (CH_2O)_{106}\,(NH_3)_{16}\,(H_3PO_4) + 53\ SO_4^{=} \rightarrow 106\ HCO_3^{-} + 16\ NH_3 + H_3PO_4 + 53\ H_2S + 106\ H_2O$$

The pore-water constitutents that are most important in fixing trace metal concentrations are O_2 and $S^=$. In the presence of O_2, Mn and Fe are oxidized to the highly insoluble +4 and +3 oxidation states, respectively. In the presence of $S^=$, Cu, Ni, and Cd (along with other trace metals) are expected to form insoluble sulfides (4). Iron and manganese are expected to be more soluble in a reducing than in an oxidizing environment. The object of this paper is to demonstrate that these expectations are followed in two environments we have studied.

One of the areas studied, Narragansett Bay, is located on the Atlantic coast roughly 300 km north[illegible] of New York. Sediments at a site called "Jamestown North," at a wa[illegible]epth of about 5 m, are largely unpolluted and heavily mixed by burrowing worms, snails, and molluscs. We have done detailed studies of pore water chemistry and benthic fluxes at this site.

Pore-water concentrations of ΣCO_2, $S^=$, NH_3, $PO_4^=$, and the metals Mn, Fe, Ni, Cu, and Cd are shown in Fig. 1 for a short core (sampled at 1-cm intervals to a depth of 15 cm) and in Fig. 2 for a long core (sampled at 5-cm intervals to a depth of 100 cm). The data presented here are from diver-collected cores. Sediment was removed from cores in a helium atmosphere. Sediment samples were centrifuged at in situ temperatures to separate out pore waters. The waters were filtered through 0.45 micron Nuclepore filters. ΣCO_2 was measured by gas chromatography; NH_3, $PO_4^=$, and nitrate, were determined by colorimetry. Mn and Fe were measured by flameless atomic absorption spectrophotometry without preconcentration, and Ni, Cu, and Cd were measured by flameless atomic absorption spectrophotometry following preconcentration by Co-APDC coprecipitation (3). Results are shown in Figs. 1 and 2.

At this site, concentrations of metabolites in pore waters are generally constant to a depth of about 25 cm as a result of burrowing activity. Metabolite concentrations are fixed at a level where input by decay is balanced by removal by the pumping activity of the infauna (which exchange pore waters and bottom waters). Occasionally, as in core 11, the concentration of metabolites actually decreases with depth, due presumably to the metabolic release rate decreasing with depth more rapidly than the pumping rate. At greater depths, in the absence of pumping, concentrations increase and upward transport is by ionic and molecular diffusion alone.

Although dissolved oxygen was not itself measured in the pore waters, the ΣCO_2 results strongly suggest that oxygen is absent at depths greater than a

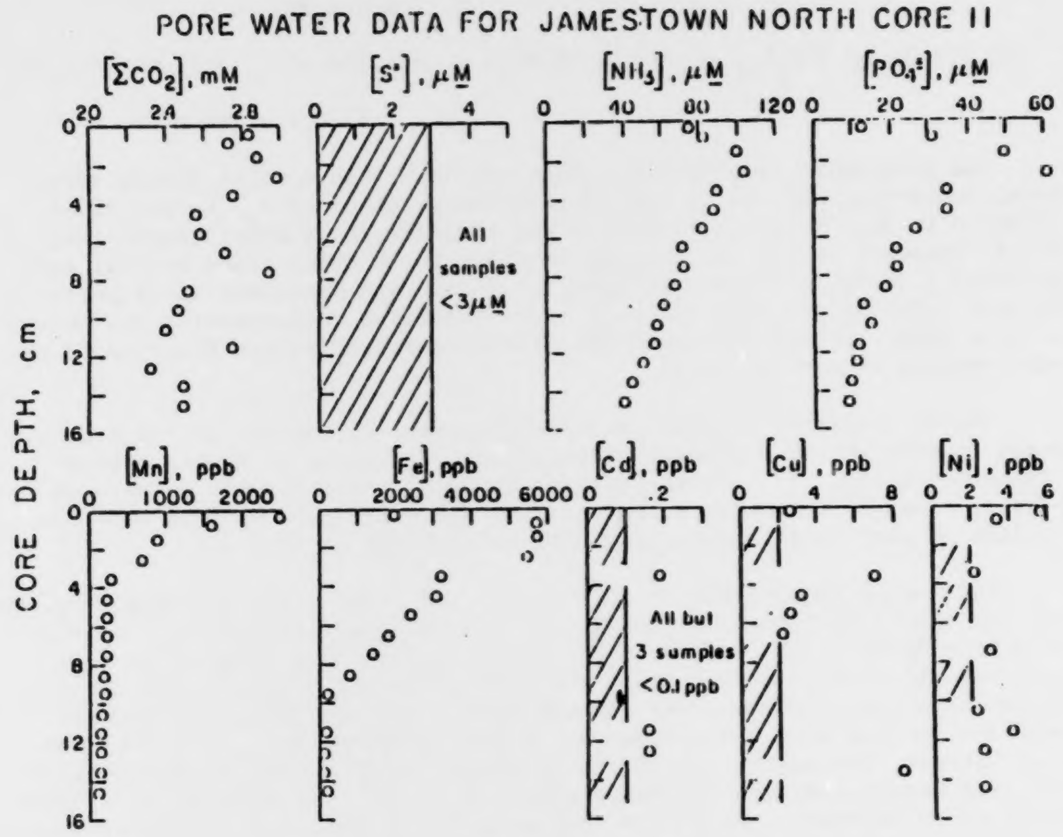


Figure 1. Concentration of ΣCO_2, $S^=$, NH_3, $PO_4^{\equiv}$, Mn, Fe, Cd, and Ni in pore waters from the top 15 cm at the Jamestown North study site (Narragansett Bay).

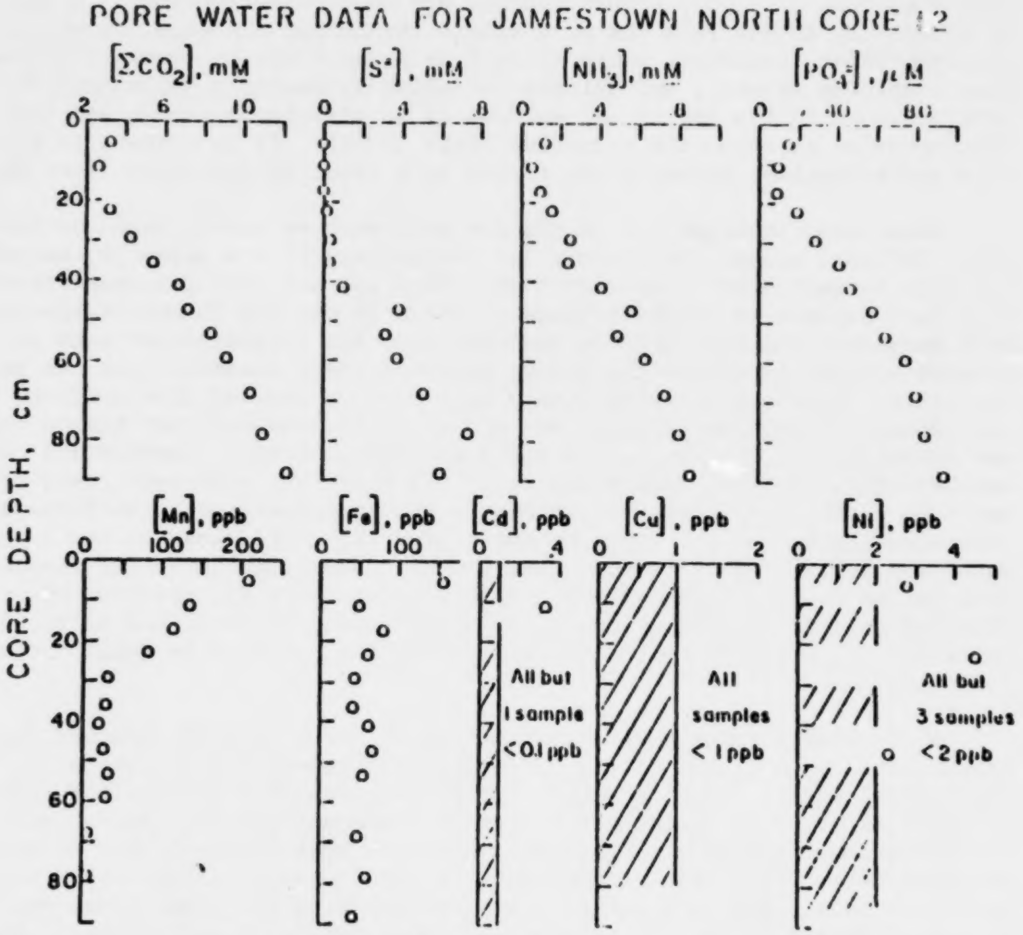


Figure 2. Concentrations of ΣCO_2, $S^=$, NH_3, $PO_4^{\equiv}$, Mn, Fe, Cd, Cu, and Ni in pore waters from the top 80 cm at the Jamestown North study site (Narragansett Bay).

few millimeters. The CO_2 concentration of bottom waters is 2.0 mM and the O_2 concentration is .15 mM. Hence, when all O_2 has been used in respiration, the CO_2 content of pore waters would rise to 2.15 mM. NO_3^- reduction (reaction 2) would result in a small additional increase (perhaps to 2.20 mM); higher ΣCO_2 concentrations probably reflect organic matter oxidation by sulfate (reaction 3). ΣCO_2 concentrations are considerably higher. Hence, O_2 is apparently absent from the pore waters throughout the core (except at the sediment-water interface, where it must be present due to downward diffusion from overlying waters), and sulfate reduction is occuring throughout the sediment column. In the top 15 cm, sulfide is so efficiently scavenged that its concentration is below the detection limit (3 μM). It is present in detectable concentrations below 20 cm, rising to a level of 600 μM at 70-cm depth.

Metal distributions are consistent with what we expect based on assumptions outlined above. In the top few centimeters of the sediment, manganese and iron concentrations are very high -- 2000 ppb and 6000 ppb, respectively. They fall rapidly to concentrations of about 20 ppb and 50 ppb, respectively. Both manganese and iron diffuse downward into the sediments and must be removed by precipitation; the phases removing these elements have not been identified, although it seems likely that iron is removed as a sulfide. Concentrations of cadmium, copper, and nickel in Narragansett Bay bottom waters are approximately 0.1 ppb, 2 ppb, and 3 ppb, respectively. Cadmium and copper concentrations in pore waters generally are below the detection limit of 0.1 and 1 to 2 ppb, respectively, presumably due to scavenging by sulfides as indicated above. Nickel concentrations generally fall close to the 2 ppb detection limit, and it is not clear whether these concentrations represent true values or only upper limits. In all cases there are spurious values (for example, Cd concentrations of 0.15 ppb in the 11 to 12 and 12 to 13 cm intervals of Jamestown North core 11), which are believed to reflect random contamination.

Pore-water chemistry was also studied in cores from the Eastern Equatorial Atlantic on a cruise of the R/V Gyre. Concentrations of nutrients, ΣCO_2, and several metals were measured. Cores were extruded in a helium atmosphere and pore waters were squeezed with Teflon Reeburgh-type squeezers. Nitrate concentrations (actually nitrate plus nitrite) were measured by a Technicon autoanalyzer. Trace metal concentrations were measured as described earlier for Narragansett Bay pore waters. Nitrate profiles for these cores are discussed by Bender et al. (1) in terms of reactions 1, 2, and 3 above. Bottom-water nitrate concentrations are about 22 μM. Pore water concentrations initially increase due to O_2-oxidation of organic matter (reaction 1). They then decrease due to downward diffusion and nitrate reduction (reaction 2). Eventually nitrate concentrations reach a level of <1 μM, at which point sulfate reduction (reaction 3) may commence. Oxygen is believed to be present from the sediment water interface throughout the depth range where $\frac{d^2(NO_3^-)}{dz^2} < 0$ (z = depth) (1). This corresponds to a depth of about 6 cm for core G76-5-10GC1 and <3 cm for G76-5-24SC. Sulfide production is believed to be zero as long as nitrate is present. Based on the low sulfide concentration (<3 μM) observed in the sulfate-reduction zone of nearby cores, sulfide is believed to be essentially absent from pore waters containing

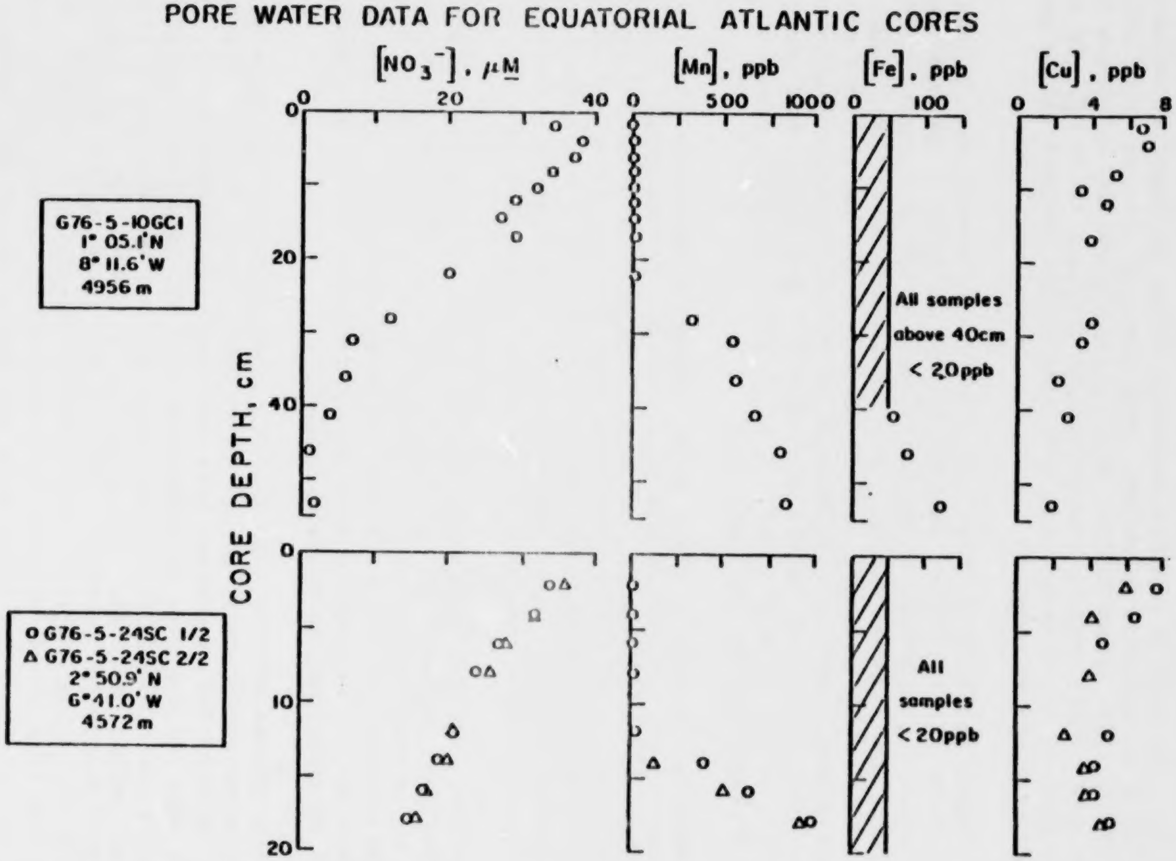


Figure 3. Concentrations of nitrate, Mn, Fe, and Cu vs. depth in two cores from the eastern equatorial Atlantic.

$\geq 5\ \mu\underline{M}\ NO_3^-$.

In core 10GC1, manganese and iron concentrations are below detection limits in the oxygen reduction zone and in the top of the nitrate reduction zone. Within the zone of nitrate decrease, below the depth at which oxygen is believed to be present, manganese concentrations rise to about 1000 ppb. In core 10GC1, iron concentrations begin rising above the detection limit at about the depth where nitrate concentrations decrease to $<2\ \mu\underline{M}$. In core 24SC, the base of the nitrate reduction zone is not reached and no rise in iron concentrations is observed.

The copper profiles in these cores are far different than in the Jamestown North cores. Copper concentrations are about 7 ppb near the sediment-water interface and decrease to about 4 ppb at a depth of 18 cm in core 24SC, and 2 ppb at a depth of 50 cm in core 10GC. The higher copper concentrations are believed to reflect copper input from degraded organic matter and skeletal debris. The absence of sulfide apparently allows copper concentrations to build to levels appreciably higher than those found in local bottom waters (probably about 0.1 ppb)(2) or in pore waters of sulfate-reducing Narragansett Bay sediments.

In summary, pore-water trace metal concentrations correlate with sulfide and apparent oxygen content in the expected way. In the oxygen reduction zone and the top of the nitrate reduction zone of equatorial Atlantic cores (10GC1 and 24SC), iron and manganese are very low and the copper concentrations far exceed bottom water values. In the middle of the nitrate reduction zone of the two Atlantic cores, the manganese concentration rises abruptly. The iron concentration increases in the sulfate-reduction zone of core 10GC1.

Dissolved iron and manganese concentrations are high in pore waters of sulfate-reducing sediments in Narragansett Bay. Cu, Ni, and Cd concentrations in these pore waters are less than or equal to values in the overlying, oxygenated waters. Cu concentrations in sulfate-reducing, Narragansett Bay pore waters are far below values in oxygen-reducing and nitrate-reducing sediments from the eastern tropical Atlantic.

Benthic fluxes of metals at the Jamestown North site in Narragansett Bay have been measured directly, according to procedure of Hale (6) and Nixon et al. (7). Results for manganese have been reported previously (5). The apparatus used for the flux determination is a PVC pipe half, sealed by plates on both ends and a flange around the base; the volume is about 27 liters and the average height is 11 cm. The apparatus is placed over the sediment and an "initial" sample is withdrawn. Three hours later, water inside the chamber is mixed by a pumping procedure and a "final" sample is withdrawn. The flux is calculated from the difference in concentrations of the initial and final samples, the length of the experiment, and the height of the chamber. While there are clearly many problems associated with these determinations, the results are believed to provide a reliable first approximation of benthic fluxes.

During the summer of 1975, benthic fluxes of metals were measured in a series of 12 experiments at the Jamestown North study site. The results are given in Table 1. Average values for the Cd, Cu, and Ni fluxes are negative, indicating that there is a net flux of these elements into the sediments rather than a flux out. Upper limits for the release of these elements may be estimated from the mean flux plus one standard deviation of the mean flux; limits on fluxes thus estimated are +.0014, +.033, and +.029 μg cm^{-2} day-1 for Cd, Cu, and Ni, respectively. These upper limits are about two orders of magnitude less than the Mn benthic flux, and about one order of magnitude less than the Fe benthic flux.

Mn and Fe fluxes are much higher than those of Cd, Cu, and Ni, but do not follow the relative pore water concentrations of Mn and Fe. The Fe concentration in the top centimeter of sediment is nearly three times higher than that of Mn, but its flux is an order of magnitude lower. This is believed to reflect rapid oxidation and precipitation of iron in the water column.

The average height of the water column in Narragansett Bay is about 10 m. From this value, average concentrations of metals, and mean values or upper limits for benthic fluxes, values (or upper limits) for the doubling time of metals may be calculated. (For reference, the flushing time of Narragansett Bay is about one month.) The doubling time calculated for Mn is about five days. Hence it is clear that diffusion out of sediments is an important source of dissolved manganese in the water column. On the other hand, the minimum doubling times of Cd, Cu, and Ni are 2 to 3 times the flushing time of the bay. Hence, diffusion out of sediments is apparently not an important source of the burden of these metals in the water column. Iron is excluded from this discussion because its distribution in the water column is not well-known.

TABLE 1. BENTHIC FLUXES MEASURED AT THE JAMESTOWN NORTH STUDY SITE AND ESTIMATED DOUBLING TIMES FOR Cd, Cu, Ni, Mn, AND Fe IN NARRAGANSETT BAY

	Mean flux and standard deviation (μg cm^{-2} day^{-1})*	Concentration of dissolved metal in Narragansett Bay	Time for benthic flux to double water column concentration
Cd	-.0029±.0043	0.1 ppb	> 71 days
Cu	-.009±.044	2.0 ppb	> 57 days
Ni	-.035±.064	3.0 ppb	> 100 days
Mn	2.1±0.8	10.0 ppb	> 4.8 days
Fe	.17±.23		

* Based on twelve determinations.

† Calculated excluding one anomalously high value believed to reflect contamination.

REFERENCES

1. Bender, Michael L., Kent A. Fanning, Philip N. Froelich, G. Ross Heath, and Valentine Maynard. 1977. Interstitial Nitrate Profiles and the Oxidation of Sedimentary Organic Matter in the Eastern Equatorial Atlantic. (In preparation.)

2. Bender, Michael L., and Christine Gagner. 1976. Dissolved Copper, Nickel, and Cadmium in the Sargasso Sea. Journal of Marine Research 34, 327-339.

3. Boyle, Edward G., and John M. Edmond. 1975. Determination of Trace Metals in Aqueous Solution by APDC Chelate Coprecipitation. In: Advances in Chemistry Series, No. 147, Analytical Methods in Oceanography, Thomas R. P. Gibb, Jr., ed., American Chemical Society. pp. 44-55.

4. Elderfield, H., and A. Hepworth. 1975. Diagenesis, Metals, and Pollution in Estuaries. Marine Pollution Bulletin 6, 85-87.

5. Graham, William F., Michael L. Bender, and Gary P. Klinkhammer. 1976. Manganese in Narragansett Bay. Limnology and Oceanography 21, 665-673.

6. Hale, Stephen. 1974. The Role of Benthic Communities in the Nutrient Cycles of Narragansett Bay. M.S. Thesis, University of Rhode Island. 129 pp.

7. Nixon, S. W., C. A. Oviatt, and S. S. Hale. 1976. Nitrogen Regeneration and the Metabolism of Coastal Marine Bottom Communities. In: The Role of Terrestrial and Aquatic Organisms in Decomposition Processes, J. M. Anderson and A. Macfayden, eds., Blackwell Scientific Publication, Oxford. pp. 269-283.

THE FATE OF METALS IN ESTUARIES*

Karl K. Turekian
Department of Geology and Geophysics
Yale University, New Haven, Connecticut 06520

INTRODUCTION

From the geochemical point of view, an estuary is a reaction vessel in which the mixing of stream water and seawater has consequences far beyond simple dilution. Streams bring more than fresh water to the basin: they are bearers of dissolved organic compounds and inorganic species; detrital material including organic matter; iron and manganese oxide grains and coatings, as well as the minerals from soil profiles. And the sea provides the well-known dissolved chemical species that make it salty. Of these, sulfate plays a special role in determining chemical pathways in the estuary, especially in relation to biological activity in the sediment column. In addition, the dynamics of estuarine circulation and the activity of benthic populations force intimate contact between the water column and the sediment pile.

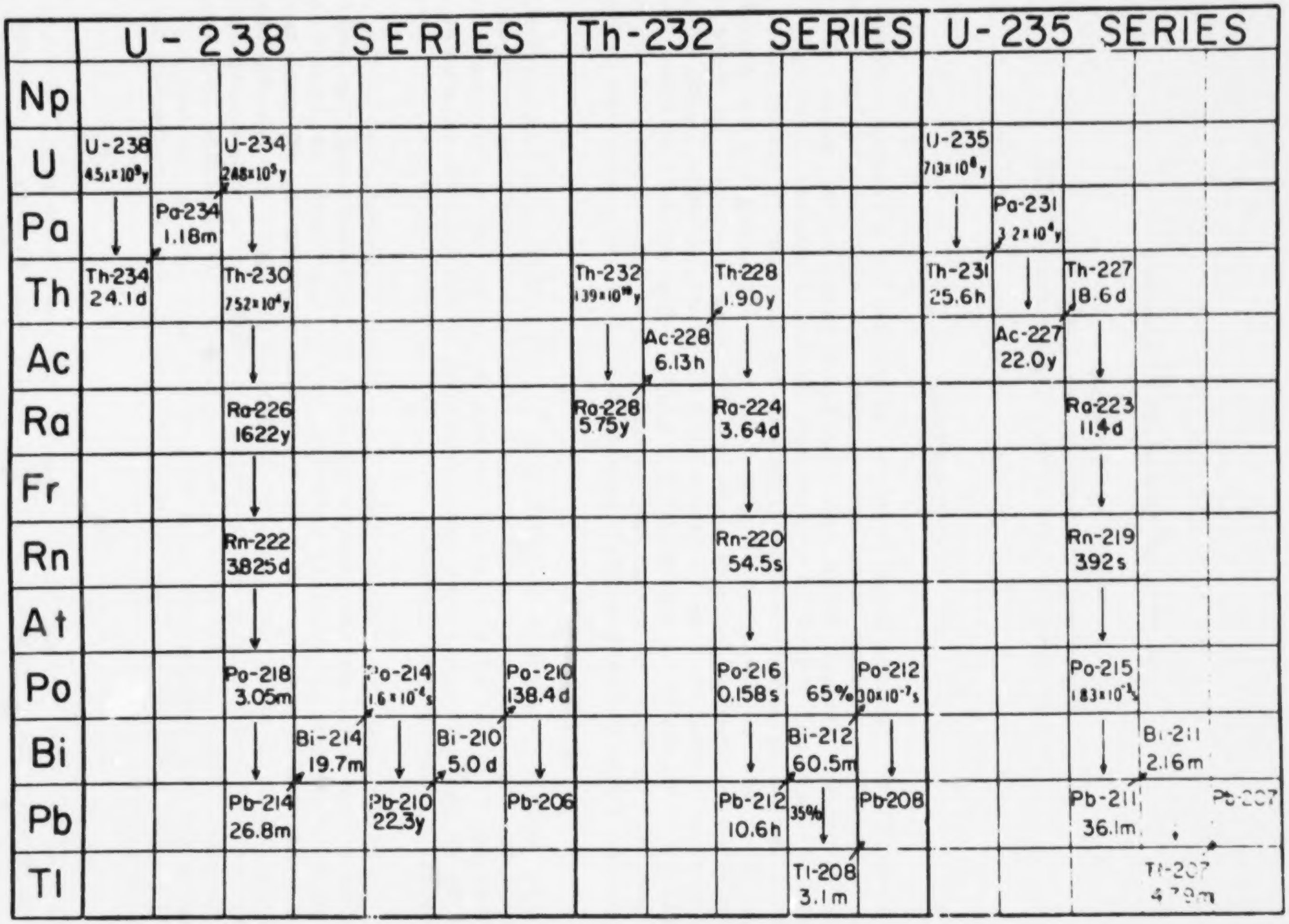
All techniques capable of helping us to understand this complex system are welcome, even when they yield results leading to diametrically opposite conclusions. For, at this point of contradiction, we can see how much our analysis of the system has been oversimplified or how we have structured too artificial a framework to represent this complex reaction vessel.

One of the most pressing problems in estuarine geochemistry is the behavior of the trace metals: stream supplies are modified, and the quality and quantity of what is actually delivered to the open ocean is determined. I think that one of the best ways to understand the behavior of trace metals in estuaries is to study the behavior of manganese, iron, and the daughters of the uranium (and thorium) decay series nuclides in the stream-estuary-ocean system. These metals provide the opportunity to determine rate constants in natural systems. We hope that these constants can be used in modelling the behavior of other elements for which data are difficult to obtain directly.

---

*To be published in "Estuaries, Geophysics, and the Environment," a report of the Geophysics Research Board of the U. S. National Academy of Science, Washington, D. C. 20418. Research supported by U. S. Energy Research and Development Administration.

TABLE 1. THE URANIUM AND THORIUM DECAY SERIES



Manganese and iron readily undergo oxidation and reduction under the conditions available in different parts of an estuarine system and are generally abundant in the sediments. The anoxic sediments in which seawater sulfate in pore waters is reduced by bacteria to form hydrogen sulfides also reduce iron and manganese in the sediment to Fe^{+2} and Mn^{+2}. As the concentrations of these ions are determined by the solubilities of their sulfides, their concentrations are quite high in pore waters--a property of manganese and iron but not of other common metal sulfides. (Manganese solubilities may also be controlled by the stability of $MnCO_3$ rhodochrosite.) The release of Mn^{+2} and Fe^{+2} into aerated waters by biological and physical mechanisms results in their oxidation to Fe^{+3} and Mn^{+4}, respectively, and their precipitation as oxides. The freshly precipitated iron and manganese oxides provide highly reactive surfaces that sequester many trace metals.

One member of the uranium decay series of interest in modelling the behavior of metals is ^{210}Pb (half life = 22 years)(Table 1). This nuclide is supplied to aqueous systems in part by the decay of ^{222}Rn mainly derived from dissolved ^{226}Ra. The atmosphere is the other source: the decay of ^{222}Rn (which continuously emanates from soils to the atmosphere) results in a supply of ^{210}Pb that is transported to ground level by precipitation.

Another nuclide in the uranium decay series, ^{234}Th, is also of value in predicting the behavior of trace metals in estuarine waters. Because it is supplied to estuarine waters exclusively by the decay of dissolved ^{238}U, and its half life is 24 days, ^{234}Th provides direct information on the systematics of the metal scavenging process in an estuary.

Part of our work on the stable trace metals is interpreted in light of experiments recently done by others. The following are some of the insights that have been gained on these systems by our group at Yale.

The Supply of Metals by Rivers

The composition of non-impacted streams results from the weathering process. Except at times of extremely high rainfall, the water in the stream channels is derived from ground water. The reactions at depth in the country rock fix the composition of the ground water supplied to the stream channel. Aerated rain water percolating through the soil loses its oxygen progressively as a result of metabolism by soil bacteria. The major reservoir of ground water is thus anoxic and provides a reducing environment that influences chemical speciation. The most important effect for trace metal transport is that, under reducing conditions, manganese and iron can be mobilized. Streams fed by these manganese- and iron-rich ground waters are oxidized and subject to precipitation. Manganese and iron oxide precipitates sometimes can be seen in massive deposits around springs, but they usually precipitate on the surfaces of the ubiquitous particles found in a running river.

The deficiency of ^{210}Pb in ground water generally (Table 2), relative to the expected supply either by rain from dissolved ^{222}Rn (mainly supported by ^{226}Ra), implies that adsorption of ^{210}Pb has occurred at depth. The trace metal nuclides can be expected generally to be subject to the same sequestering action. After steady state between dissolution and adsorption is estab-

TABLE 2. SUMMARY OF BEHAVIOR OF ^{210}Pb IN GROUND WATER REGIMES BASED ON DATA*

RAIN Pb^{210} = 10 dpm/ℓ	
EVAPORATION-TRANSPIRATION = 50%	**LAND SURFACE**
INFILTRATION Pb^{210} = 20 dpm/ℓ	
	WATER TABLE
Pb^{210} = 0.4 dpm/ℓ Ra^{226} = 1 dpm/ℓ	**SHALLOW GROUND WATER**
Pb^{210} = 0.04 dpm/ℓ Ra^{226} = 10 dpm/ℓ	**DEEP GROUND WATER**
T = 1 Month	

---

*From R. B. Holtzman (1964) in The Natural Radiation Environment, (J.A.S. Adams and M. Lowder, eds. Univ. of Chicago Press.)

lished, however, a measurable flux of metals to the stream may occur although it may not be seen in the ^{210}Pb concentration. On the basis of ^{210}Pb estimates in ground water, the mean residence time relative to adsorption is less than a month. Some of this removal may be accomplished by roots of plants and trees that then transfer ^{210}Pb (as well as stable trace metals) to the surface where they become part of the plant litter. Thus, as rock is disintegrated by the action of soil organisms, producing organic acids and carbonic acid, some of the metals are absorbed by the vegetation. Subsequent decay of this vegetal material provides an organic-rich material commonly called top soil. This top soil is the repository of seasons of accumulation of vegetal debris processed and reduced in volume by soil organisms. The residual organic material itself is a strong sequesterer of trace metals. Using ^{210}Pb derived from atmospheric precipitation as a tracer, Benninger et al. (2) have shown that virtually every bit of the ^{210}Pb supplied by precipitation is retained by the top soil (Table 3).

TABLE 3: ATMOSPHERIC FLUX OF ^{210}Pb IN THE EASTERN U.S. BY DIRECT MEASUREMENT AND ACCUMULATION IN GROUND LEVEL LONG-TERM REPOSITORIES*

Location	flux $dpm/cm^2/yr$	Type of Measurement
New Haven, Conn.	1	precip. & dry fallout
East Haven, Conn.	1	salt marsh profile
East Haven, Conn.	0.8	soil profile
Cook Forest St. Park, Pa.	1	soil profile
Maryland	1.2	soil profile

*Compiled by Benninger et al. (3)

By the erosion of its banks, a tributary system transports sections of the soil profile, including the top soil with its sequestered metals. A material balance calculation of ^{210}Pb in the drainage basin of the West Branch of the Susquehanna River indicates that this nuclide has a mean residence time of about 2000 years in the soil relative to transport by streams (7).

As a stream moves its burden of minerals and organic-rich detritus to the sea, it is continuously fed by ground waters that supply dissolved materials. However, additional chemical changes can occur in the channel itself. The river bed is an environment where biological activity can deplete oxygen in pore waters and thus supply soluble manganese and iron to the stream. This is most effective in deeper and wider parts of the stream channel and causes precipitation of oxidized manganese and iron on the suspended material in the stream in a continuous manner down its course.

The act of cycling manganese and iron in the river, as well as the supply of additional quantities of these elements in soluble form from ground water, results in an efficient scavenging of trace metals from the stream onto particles. In the case of the natural tracer ^{210}Pb, it can be shown that its mean residence time in solution in streams is about one day, and seems to be coupled directly to manganese precipitation (7). Thus the rate constant for manganese precipitation (and possibly iron) may determine the rate constant for the removal of many trace metals from solution. As manganese is resupplied to the stream for reducing sediments along its course, a fraction of the precipitated metals may also be released, thus providing a steady-state soluble concentration of each of the metals. The low relatively constant concentrations of many trace metals in streams may be explained by this steady-state process.

The trace element concentrations in the particles in streams are related to both the manganese concentration and the organic matter concentration. They are unrelated to the formal ion exchange capacities of the clay minerals typically supplied from weathering profiles. Our early experiments in adsorption and desorption of trace metals on clay minerals in freshwater and seawater systems thus are incapable of explaining the major controls on trace element transport as seen in real streams. It is doubtful if increasingly sophisticated in vitro experiments of this kind will provide any new insights into trace metal behavior in natural aqueous systems.

The particles in streams also act to modify the stream composition when artificial injections of soluble trace metals occur (10). In the Naugatuck River of Connecticut (a tributary of the Housatonic), the Ni, Co, and Ag concentrations drop at least an order of magnitude from the point of injection of industrial metal-rich acid wastes to a point 1 km downstream (Fig. 1). The metals sequestered on particles are transported to the estuary. A striking example of this is seen in the high trace metal concentrations found on suspended particles in the Rhine River as it transects The Netherlands (8).

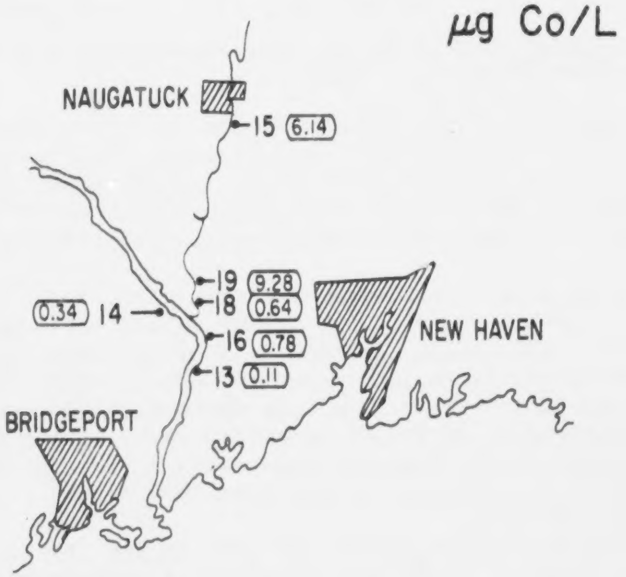


Figure 1. The distribution of "dissolved" cobalt in the Naugatuck-Housatonic river system. The Naugatuck River is heavily impacted by industry and high in dissolved metals. The concentration decreases away from the source of impact as the result of adsorption on particles.

In summary, we see that the burden of trace metals supplied to an estuary by streams comes primarily on particles. This in turn is related to the organic and manganese concentrations of the particles. By analogy with the behavior of ^{210}Pb in such systems, it is obvious that organic and manganese oxide phases are strong sequesterers of trace metals. What occurs, then, as this assemblage reaches the sea?

The Freshwater-Seawater Encounter

The physical boundary where a stream encounters seawater is hardly a simple one. In most places, the action of the tides continuously changes the encounter configuration; any strong change in stream runoff, on the one hand, or the response of the sea to storms, on the other, has profound effects on this interface.

Two diametrically opposite processes involving trace metals may occur at the freshwater-seawater boundary:

(1) The precipitation of iron and manganese, and some other elements such as phosphorous, aluminum, and titanium, has been shown to occur in both field and laboratory experiments. This is ascribed to the formation and flocculation of colloids as the increased ionic content of the saltwater alters charge distributions (9, 4).

(2) The release of metals from particles at the seawater interface has also been invoked to explain certain field observations (5). This process is compatible with laboratory experiments in which trace metals adsorbed from fresh water on clay minerals have been shown to release them as the total cationic concentration of the solution increases. This process exists most strikingly as the hydrogen ion concentration increases, but the encounter with seawater does not normally decrease the pH of solutions. We have seen, moreover, that the trace element burden must be carried by the organic- and manganese-rich phases, not by clay minerals.

The field evidence for release of trace metals in the estuarine system is the observation that suspended particles in some European estuaries decrease in trace metal concentrations as the salinity increases (8). The exact method of release is not specified but appears to be the destruction of the metal-bearing phases rather than simple desorption. Such field experiments depend, of course, on the assurance that only the stream-borne particles are involved in chemical changes occurring progressively seaward. If non-indigenous sediments are transported into the estuary from the open sea, the change in composition of particulate matter thereafter may be due to dilution--not chemical gain or loss on the stream-originating particles alone. This is difficult to ascertain since the mineralogy, in a strict sense, will not be different over a broad region of a shelf area, thus confounding the identification of sources. More importantly, the metal-bearing phases cannot be diagnostically identified; therefore, a mixing curve of open ocean particles poor in such phases with stream-borne particles rich in them will not be visible mineralogically. Indeed the definition of the mixing may well be the distribution of trace metals on the particles! It is clear that analysis of particles for metals alone will not provide a singular answer to this problem.

Our study of the encounter of the Housatonic River with Long Island Sound at one time seemed to provide direct evidence for release of metals from particles at the boundary between freshwater and seawater. Both the Housatonic and the open waters of Long Island Sound showed much lower concentrations of cobalt, nickel, and silver than the mouth of the Housatonic (Fig. 2). Although these results might still be interpreted as showing release of metals, another explanation seems to be better.

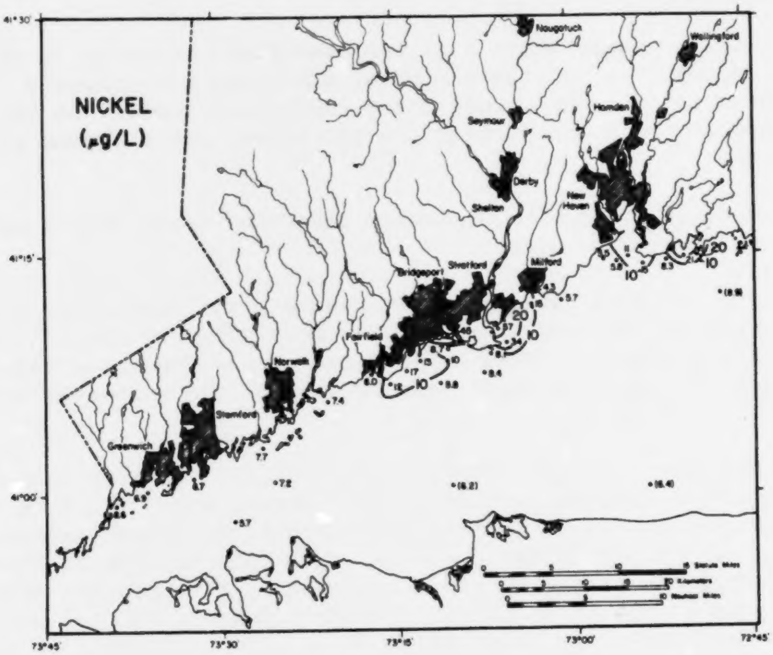


Figure 2. The nickel concentration increases sharply at the mouth of the Housatonic River. This is probably due to the release of metals from particles at the freshwater-seawater interface. The mechanism may be enhanced, if not actually controlled, by the presence of salt marshes.

The mouth of the Housatonic River is marked by a very large salt marsh area. The tidal range in this region is almost 2 meters--the largest amplitude in Long Island Sound. In salt marshes (as in marine deposits), the storage of metals is related to indigenous reducing conditions. Sulfate in pore waters is reduced to sulfide, which is then sequestered by the ubiquitously available iron found in mineral surfaces. At low tide, the top layers of the marsh are aerated; at times of rainfall at low tide especially, the sulfide phases in the marsh are oxidized and sulfate and associated metals are solubilized. As the tide comes in, the process is terminated and trapping of trace metals can reoccur. Metal-rich particles from the streams are continuously trapped in the salt marsh, and atmospheric precipitation adds an additional burden. Thus a concentration halo of certain trace metals in seawater is maintained around the salt marsh environs.

A similar process has been shown to occur on a horizontal scale in the Scheldt estuary by Wollast (11). There, reduced iron derived from the sediment is transported seaward with sulfide particles in anoxic waters. As the aerated open ocean water is encountered, the trace-metal-bearing sulfide phases oxidized. A marked increase in dissolved copper concentration occurs simultaneously with a sharp decrease in dissolved iron as oxidation, and precipitation of the oxide occurs. The pattern of trace-metal release or precipitation occurring at a river mouth thus can be a complicated one.

We must discuss one additional factor influencing the fate of metals at the stream-estuary boundary. That is the hold-up time at the encounter. The stream encountering the sea is essentially ponded to some degree before it overflows or mixes with its saline barrier. During its holdup, reactions typical of reservoir situations can occur. Metals (as well as silicon) are removed from the water column, as seen in the Connecticut River (Fig. 3). After the water leaves the system, by breaching or mixing with the salty estuarine barrier, it essentially mixes conservatively with the ambient estuarine waters. The influence of the tides appears to be paramount in providing the mechanism for holding up the stream water. It is not unreasonable to expect that, in stream systems experiencing small tidal effects, the trace metal concentration patterns during mixing are essentially conservative.

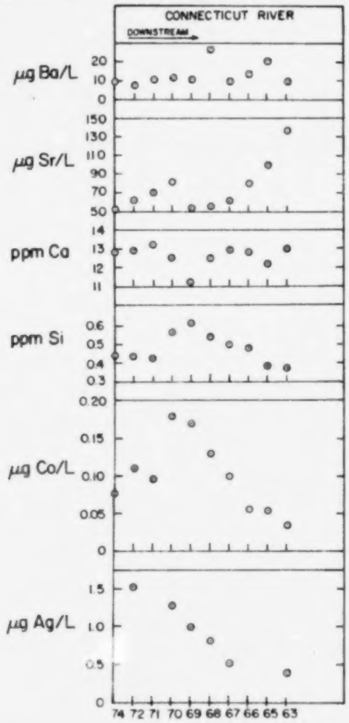


Figure 3. Both metals and silicon decrease in concentration in the freshwater tidally affected parts of the Connecticut River. This can be ascribed to a reservoir effect based on width of the river mouth and tidal cycling.

The Larger Estuarine Mixing Basin

The large estuarine system is an important arena for further modification of the water before it becomes a part of the open ocean system. Such systems as Long Island Sound, Chesapeake Bay, and the Baltic Sea, although different in many ways, share the common property of being very large mixing basins. A mixing basin is subject to many of the same effects controlling the fate of trace metals as streams and the stream-seawater encounter discussed above. The extent of the modification depends on the length of time distinctively estuarine processes have to act on the water column. A fast flushing rate (i.e., completed in days) essentially makes the estuary a conduit. A slow flushing rate (completed in weeks) makes it a standing body of water with special properties due to the presence of seawater and tides.

It is the combination of biological activity in the sediment column and physical movement of the waters by storms and tidal action that makes the estuarine basin a particularly active region chemically.

Using ^{210}Pb from atmospheric precipitation primarily and ^{234}Th from *in situ* production from dissolved ^{238}U as tracers, we are able to identify possible mechanisms capable of modifying estuarine water composition. The work on ^{234}Th in Long Island Sound by Aller and Cochran (1) clearly shows that its residence time in the water column is about one day. This is the same order of magnitude of time as that for ^{210}Pb in streams. The fact that no dissolved ^{210}Pb can be identified in Long Island Sound (Fig. 4) implies that it too is rapidly removed in estuarine systems, resembling ^{234}Th in behavior. We will assume that this is indeed true and search for an appropriate mechanism.

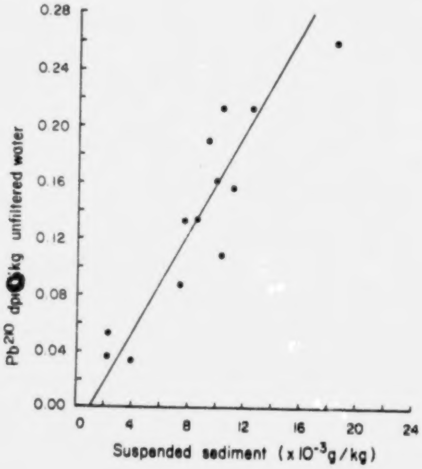


Figure 4. A plot of the total ^{210}Pb activity in Long Island Sound water versus the amount of suspended sediment, indicating virtually no dissolved ^{210}Pb in the Sound.

It can be shown on the basis of material balance calculations that plankton cannot be important in transferring ^{210}Pb (and presumably ^{234}Th) to the estuarine floor. It does not seem likely that clay minerals are important scavengers since, in the more propitious freshwater system, they do not seem to be very effective agents.

The most likely agents appear to be the manganese and iron released from the reducing sediments as they are oxidized in the water column and form fresh precipitates. The precipitates deposit on suspended particles and there act as scavengers for a large number of trace metals. On return to the ocean floor, settling particles are reworked into the sediment by burrowing organisms. When the manganese and iron are recycled by the reduction-release-oxidation-precipitation steps, the trace metals carried down by the process mainly remain trapped in the sediment column, as seen by the material balance calculation for ^{210}Pb. Only when trace metal bearing sulfide particles are oxidized in the water column is there a refluxing of the associated metals to the waters again.

By this process, an extended residence of water in an estuarine basin results in a scavenging of the metals from the water column into the sediments.

Some of the finest grained manganese and iron oxide particles, with their associated trace metals, will be swept to sea. This seems to be verified by the material balance studies on man-made ^{55}Fe reported by Labeyrie et al. (6). The deficiency in some coastal sediments may be due to loss to the open ocean from the estuarine system. This manganese and iron could be a prime source of supply for the ubiquitous ferromanganese nodules in deep ocean deposits.

REFERENCES

1. Aller, R.C., and J.K. Cochran. 1976. ^{234}Th/^{238}U Disequilibrium in Near-shore Sediment: Particle Reworking and Diagenetic Time Scales. Earth Planet. Sci. Lett., v. 29, p. 37-50.

2. Benninger, L.K. 1976. The Uranium-series Radionuclides as Tracers of Geochemical Processes in Long Island Sound. Ph.D. Thesis, Yale University, New Haven, Connecticut.

3. Benninger, L.K., D.M. Lewis, and K.K. Turekian. 1975. The Use of Natural Pb-210 as a Heavy Metal Tracer in the River-estuarine System. In: Marine Chemistry in the Coastal Environment. T.M. Church, ed. Symp. Ser. 18, Am. Chem. Soc., Washington, DC. pp. 202-210.

4. Boyle, E.A. 1976. The Marine Geochemistry of Trace Metals. Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Massachusetts.

5. Kharkar, D.P., K.K. Turekian, and K.K. Bertine. 1968. Stream Supply of Dissolved Silver, Molybdenum, Antimony, Selenium, Chromium, Cobalt, Rubidium, and Cesium to the Oceans. Geochim. Cosmochim. Acta 32, p. 285-298.

6. Labeyrie, L.D., H.D. Livingston, and V.T. Bowen. 1975. Comparison of the Distributions in Marine Sediments of the Fallout-derived Nuclides ^{55}Fe and ^{239,240}Pu: A New Approach to the Chemistry of Environmental Radionuclides. In: Proceedings ERDA/IAEA International Symposium on Transuranium Nuclides in the Environment, San Francisco.

7. Lewis, D.M. 1976. The Geochemistry of Manganese, Iron, Uranium, Lead-210, and Major Ions in the Susquehanna River. Ph.D. Thesis, Yale University.

8. Martin, J.M. 1971. Contribution a l'Etude des Apports Terrizenes d'Oligoelements Stable et Radioactifs a l'Ocean. Ph.D. Thesis, University of Paris, Paris, France.

9. Sholkovitz, E.R. 1976. Flocculation of Dissolved Organic and Inorganic Matter during the Mixing of River Water and Seawater. Geochim. Cosmochim. Acta 40, p. 831.

10. Turekian, K.K. 1971. Rivers, Tributaries and Estuaries. In: Impingement of Man on the Oceans, D.W. Hood, ed. John Wiley and Sons, Somerset, New Jersey. pp. 9-73.

11. Wollast, R. 1975. Paper presented at IUGG, Grenoble, France, Sept. 1975.

THE STRUCTURE OF ARSENIC AND STIBIUM FIELDS IN THE CARIBBEAN SEA

A. I. Ryabinin and A. S. Romanov
Physical-Chemical Institute, Ukraninian S.S.R. Academy of Sciences,
Sevastopol, U.S.S.R.

Studies of arsenic and stibium fields in waters of the Atlantic and Pacific Oceans (1-3) reveal their complicated structure, generally governed by that of hydrological fields. Both elements, although chemical analogs, are distributed in the ocean, independent of each other.

Variations of arsenic and stibium content are great in the studied fields; therefore, the natural background of both elements in the oceans cannot be characterized by their average concentration values only.

The Caribbean Sea has a rather complicated hydrological structure. At the same time, the natural background of arsenic and stibium in seawater is not yet known. Only single determinations of stibium are known (4).

In July 1971, an investigation of arsenic and stibium was carried out along the Mona Strait-Venezuelan coast section. Simultaneously, Ganson and Paranichev (Marine Hydrophysical Institute of the Ukrainian S.S.R. Academy of Sciences, Sevastopol) performed hydrological operations on the same section.

Water samples for analysis were taken from hydrological bathometers. Investigated elements from the analyzed samples were concentrated by coprecipitating with ferric hydroxide (III). Arsenic and stibium of precipitate were determined by an instrumental neutron activation method, using the routine procedure (5).

Ninety-five water samples have been analyzed at five hydrochemical stations with two parallel ones. Figs. 1 to 3 demonstrate results of investigations by a diagram of the arsenic and stibium concentration distribution and values of their ratio.

Hydrological investigations of the section made it possible to identify several water masses.

A surface water mass had high temperature and salinity, reaching values of 27.0° to 28.8°C and 34.7 to 36.0 °/oo, respectively. Below this water mass, a subtropical subsurface water mass with a high salinity core was located at a depth of 75 to 200 m (36.91 to 36.95 °/oo). A subantarctic water mass with an intermediate minimum of salinity (∿34.8 per cent) and a typical temperature of 5° to 6°C was found at 600-900 m depths. All water masses observed in this section had a characteristic north-south slope of isohalines. For instance, salinity maximum of the surface layer in the south was situated at 50 to 75 m depths, and in the north, at a depth of 150 to 200 m. In this section, the entire deep portion of the sea was filled with water of uniform salinity (∿35.0 ^{o}/oo).

DISCUSSION

Arsenic Field

In Fig. 1, the arsenic field is divided by isolines of concentrates 5 and 10 g As/ℓ into three fields having the following limits of concentrations:0.7-5 µg/ℓ, 5-10 µg/ℓ, and 10-39 µg/ℓ. In this section, the arsenic content ranges widely from 0.7 to 39 µg/ℓ. Non-monotony of the arsenic distribution is characteristic of the entire field. The position of fields with characteristic concentrations of arsenic is in good agreement with a structure of the hydrological field.

Generally, the arsenic content does not exceed 5µg/ℓ in surface waters. Fields with concentrations up to 10µg As/ℓ are traced only in the southern portion of the section.

A subsurface subtropical mass has also low values of arsenic concentrations (<5µg/ℓ). An exception to the rule was observed at a shallow water (520 $\overline{\text{m}}$) station in the northern portion of the section where arsenic was found to be 11 to 37µg/ℓ at 60 to 100 m depths. High concentrations of arsenic are characteristic of water mass cores identified from salinity.

Generally, the subantarctic water mass (600 to 900 m) also has low arsenic content though there are centers in which concentrations exceed 10µgAs/ℓ in the core.

It is particularly interesting to note that the arsenic distribution in deep waters (>1000 m) is characterized by constant salinity and is non-uniform. In these waters, a region with high arsenic concentrations (10 to 39µg/ℓ), and two regions with low concentrations (2 to 4µgAs/ℓ), are well marked.

These data indicate that deep waters are, to a certain extent, differentiated according to a factor such as arsenic concentration. The nature of such differentiation can be revealed by special investigations. A similar picture is observed at the same depths in the tropical Atlantic (1).

Non-uniformity and non-monotony of the arsenic distribution in the section are also evident from Table 1, which contains the average values of concentrations for water layers of 0 to 100 m, 100 to 500 m, 0 to 500 m, 500 to lower level, 0 to lower level.

The highest content of arsenic was found in deep-sea layers (below 500 m). Despite a comparatively small extension of the section (∿270 mi), the average arsenic concentrations vary noticeably from station to station. The

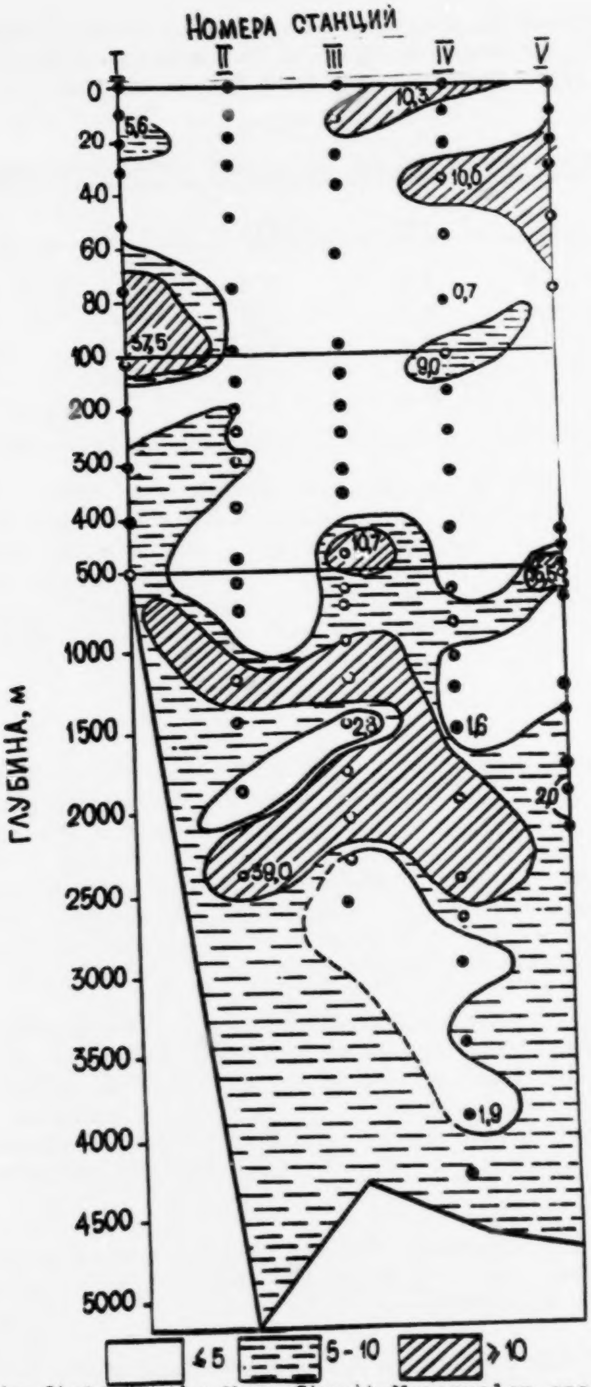


Figure 1. Arsenic field in the Mona Strait-Venezuelan coast section: solid lines, isolines of arsenic concentrations of 10 μg/ℓ; dash lines, isolines of arsenic soncentrations of 1 μg/ℓ; figures in field, values of arsenic concentrations (μg/ℓ).

arsenic content appears to increase in waters of coastal stations. Thus, when moving from station I towards station V, the average concentration of arsenic in 0 to the 500-m layer decreases only as far as station IV.

TABLE 1. THE AVERAGE VALUES OF ARSENIC CONCENTRATIONS (μg/ℓ).

Station number: Layer, m	I	II	III	IV	V	Entire section
0-100	9.6	3.3	3.4	5.3	4.4	5.2
100-500	6.0	4.4	5.0	3.0	6.8	5.0
0-500	8.1	3.8	4.2	4.0	5.2	5.1
500-lower level	--	12.5	9.2	6.6	6.5	8.7
0-lower level	8.1	6.9	6.3	5.2	5.8	6.5

On the basis of the above data, one can draw an important conclusion: the average values of arsenic concentrations in the Caribbean Sea cannot characterize its natural background content. The arsenic field has a complicated structure in the Caribbean Sea. Variations of the arsenic content are great (they reach multiplicity 55). Therefore, only the arsenic distribution field can serve as a characteristic of the background content of this element.

Stibium Field

In Fig. 2, the stibium field is divided by isolines of concentrations 0.5 and 1.0 μgSb/ℓ into three regions. The region of maximum concentrations (1.0 to 1.5 μgSb/ℓ) is not great. It is observed at a shallow water station (Station I) as separate patches and at station III as one patch at a depth of more than 1500 m. The region of minimum concentrations contains 0.1 to 0.5 μgSb/ℓ. The character of the location of regions with different contents of stibium is indicative of the fact that this element is also distributed non-uniformly and non-monotonously throughout the section.

The structure of the stibium field is in good agreement with that of water masses. Judging from the run of isolines, the 500m surface water column resembles a laminated structure. Alternation of water layers with different contents of stibium is observed here. Like some isohalines, a number of isolines also have a north-south slope. This structure of stibium field indicates that separate water masses can be characterised by the value of stibium concentrations.

Deep waters of the Caribbean Sea are non-uniform as well. Regions of high and low concentrations of stibium are observed here, and the run of isolines has a distinctive feature.

Distribution of the average values of stibium content for conventional water layers (0 to 100 m, 100 to 500 m, 0 to 500 m, 500 m-lower level, 0 to lower level) is shown in Table 2.

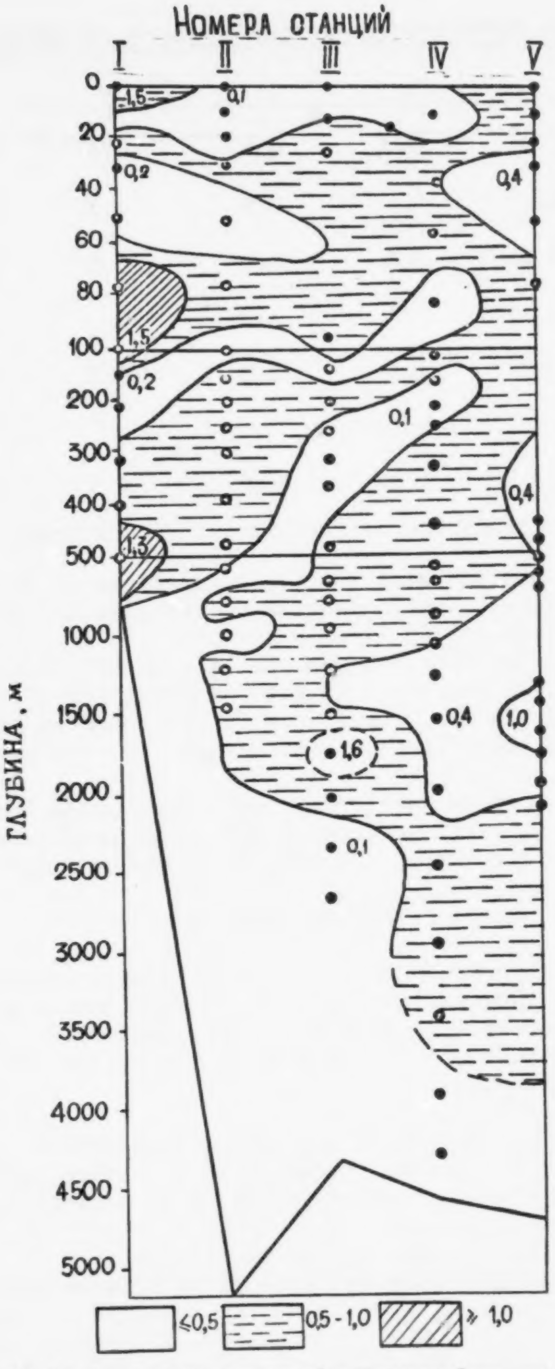


Figure 2. Stibium field in the Mona Strait-Venezuelan coast section: solid lines, isolines of stibium concentrations of 0.5 μg/ℓ; dash lines, isolines of stibium concentrations of 1 μg/ℓ; figures in field, values of stibium concentrations.

TABLE 2. THE AVERAGE CONCENTRATIONS VALUES OF STIBIUM (μg/ℓ).

Station number: Layer, m	I	II	III	IV	V	Entire section
1	2	3	4	5	6	7
0-100	0.8	0.4	0.6	0.5	0.6	0.6
100-500	0.7	0.7	0.5	0.5	0.4	0.55
0-500	0.8	0.5	0.5	0.5	0.5	0.6
500-lower level	-	0.5	0.7	0.5	0.5	0.55
0-lower level	0.8	0.5	0.6	0.5	0.5	0.6

Distribution of the weighted mean concentrations of stibium over three layers at four of five stations investigated was also non-uniform. In fact, weighted mean concentrations of stibium are the same for deep-water stations. High concentrations of stibium are typical of a shallow-water station (Station I), as noted in analysis data in Fig. 2. Therefore, the average concentrations of stibium in the entire section of separated layers are equal to the average concentration of the element in the sea (0.6 μg/ℓ).

Thus, the determined non-uniformity of stibium distribution (concentration variations of 0.1 to 1.5 μg/ℓ) does not allow us to characterize the background content of stibium in the sea, using the average concentration.

The Field of Relative Values of As (μg)/Sb (μg)

As concentration/ Sb concentration ratios, characterizing the relative distribution of these elements, are calculated from the data of Figs. 1 and 2. Based on the calculated data, a diagram is constructed of the distribution of As/Sb (Fig. 3) with isolines 5, 10, and 20, which divide the field of the diagram into four regions.

It is evident from Fig. 3 that the core of subsurface subtropical water mass (Stations III and IV) can be traced quite well from As/Sb values (5). Regions containing high values (34 to 46) of As/Sb were in deep seawater (>1000 m).

Previously, (1) As/Sb values equal to 20 to 50 were observed at the same depths in the Atlantic Ocean.

The above data indicate that arsenic and stibium are distributed independently of each other in the Caribbean Sea. As/Sb values vary from 1.5 to 50; therefore, the average value of As/Sb cannot characterize the ratio of arsenic to stibium in the Caribbean Sea.

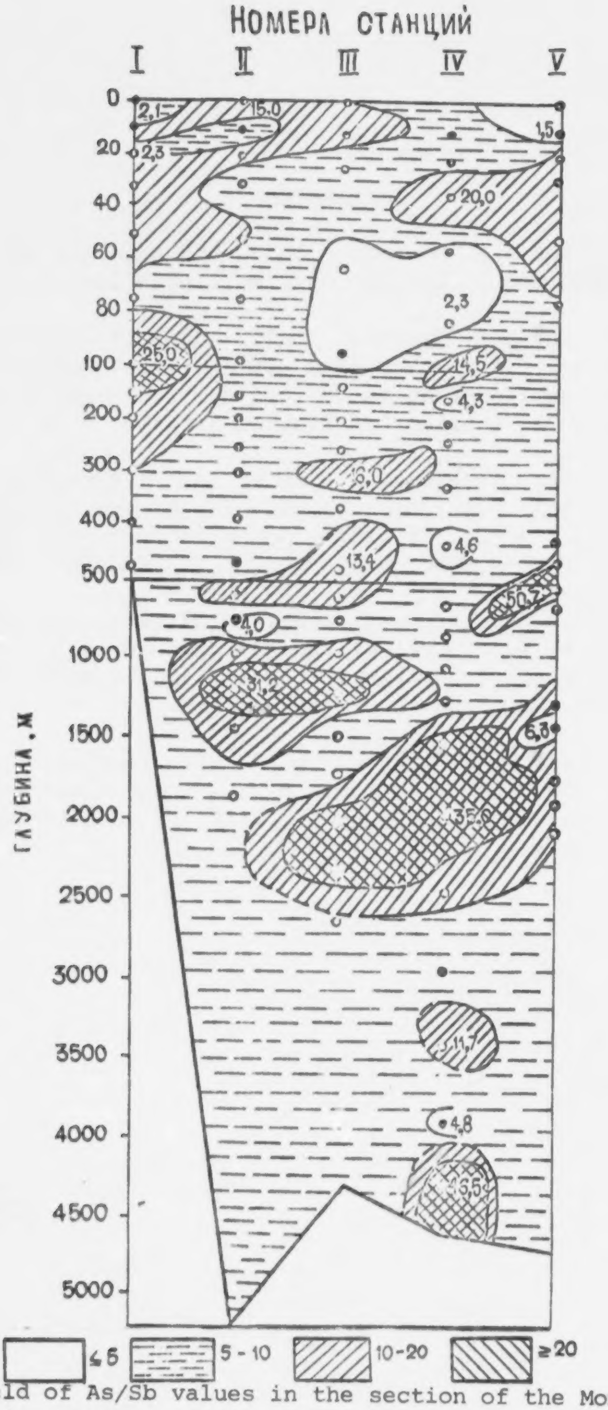


Figure 3. The field of As/Sb values in the section of the Mona Strait-Venezuelan coast: solid lines, isolines of As/Sb values figures in the field, As/Sb values.

REFERENCES

1. Ryabinin, A.I., and A.S. Romanov. 1973. Arsenic and Stibium in the Tropical Atlantic. Geochemistry, no.2. (In Russian).

2. Ryabinin, A.I., and A.S. Romanov. 1975. Arsenic and Stibium in the Equatorial Pacific. In: Marine Hydrophysical Research, no.4 (71), Sevastopol, published by the MHI of the Ukrainian S.S.R. Academy of Sciences. (In Russian, English abstract).

3. Romanov, A.S., and A.I. Ryabinin. 1976. An Investigation of Arsenic and Stibium in the Atlantic Ocean. In: Marine Hydrophysical Research, no.1 (72). Sevastopol, published by the MHI of the Ukrainian S.S.R. Academy of Sciences. (In Russian, English abstract).

4. Shuts, D.F., and K.K. **Turekian.** 1969. Studies of the Geographic and Vertical Distribution of Some Scattered Elements in Seawater by the Method of Neutron Activation Analysis. In: G.Mero, Mineral Resources of the Ocean, M., Progress. (In Russian).

5. Ryabinin, A.I., and A.S. Romanov. 1972. Neutron Activation Determination of Arsenic and Stibium in Oceanic Water with their Preliminary Concentrating with Ferric Hydroxide (III). Journal of Analytical Chemistry, no.1 (In Russian).

CHEMICAL FORMS OF MERCURY IN MARINE WATERS

A. K. Prokof'yev
State Oceanographic Institute
Moscow

One of the most characteristic properties of seawater is the constancy of its chemical composition, which historically has developed very slowly. Because of their enormous size, the world's oceans, until the middle of the 20th century, accepted with relatively few ill effects all the waste from human economic activity. It is only in the last 10 to 20 years, when this activity assumed a global scale, that a number of regions began to manifest symptoms of a disrupted ecological equilibrium and cases of poisoning for both man and representatives of the marine fauna.

Mercury is one of the most noxious substances discharged by man into the ocean because of its effect on vital biochemical processes. It should be noted that the attention of researchers and society has only recently been drawn to the toxic effects of mercury (and heavy metals in general) in the natural environment after massive mercury poisoning in Japan (Minamata's disease).

In the marine environment mercury is present in the water in suspended and colloidal particles, in bottom sediments, and in animal and plant organisms. It is distributed by very complex and little-understood mechanisms as a result of chemical, physical, physiochemical and biological processes which supplement each other, compete and intertwine, but at the same time differ considerably. The transformations can be so profound that they involve a change in the oxidation state of mercury.

At the present time available chemical data and phenomenological models do not permit an adequate prediction of the distribution of traces of heavy metals and, in particular, mercury in natural waters, as they constitute very complex electrolytic solutions including a variety of inorganic and organic substances. Although metal traces enter natural waters as a result of the weathering of rocks and volcanic activity, man introduces considerable amounts of these metals in certain regions. As soon as the rate of penetration of traces of metals or their compounds into the water system exceeds the natural cycle, pollutants may appear or unfavorable ecological effects develop. These effects have already been observed in certain regions of inland and coastal seawaters of industrially advanced countries as a result of the discharge of metals or by the combustion of fossil fuels and production of cement. The dumping of industrial, municipal, and agricultural waste waters containing a variegated mixture of variable composition of chemically and biologically active inorganic and organic substances has resulted in varied degrees of pollution.

In seawater, heavy metals can be adsorbed and bound chemically by suspended and colloidal particles which are always present in it. These equilibrium processes, which depend mainly on the concentrations of the dissolved metals, their forms, other cations and anions, as well as on the amount of these particles and their chemical and adsorption properties, have been inadequately studied. Therefore, in this paper we will only consider soluble forms of mercury and will omit numerous models for describing the distribution of mercury among various dissolved complexes as it is impossible to confirm them experimentally. This problem is mainly due to the lack of data on the equilibrium constants between mercury ions and various ligands and on the activation energy of the reacting components.

Mercury exists in nature, and in seawater in particular, almost exclusively in the divalent state. However, it is also found in very limited amounts in the unoxidized (metallic) and formally univalent forms. These three forms of mercury are related by the reversible disproportionation reaction as follows:

$$Hg_2^{2+} \rightleftharpoons Hg^0(\ell) + Hg^{2+}$$

with the equilibrium constant $K = (Hg^{2+}{}_2) = 6.0 \cdot 10^{-3,2}$ which shows a marked shift of the equilibrium to the left. However, this equilibrium can be very easily shifted to the right by many reactions which tie up Hg^{2+}; for example S^{2-}, OH^-, Cl^-, and NH_3, whose concentrations in seawater substantially exceeds that of mercury. For this reason, compounds of Hg_2^{2+} will be practically nonexistent in seawater.

Metallic mercury is usually present in seawater, where its solubility is 23.6 and 54.9 μg/ℓ at 10°C and 25°C, respectively (30), and where it penetrates from air in which it is always present in vanishingly low concentrations, and also as a result of direct chemical and biological reduction of Hg^{2+} ions in seawater. It should be noted that it dissolves much better in hydrocarbons than in water. This fact may have unfavorable after effects because of the concentration of mercury in oil-polluted regions. Mercury reacts in nature at very slow rates with a number of nonmetals and, what is particularly important, with oxygen, to form mercury oxide, thus changing to a much more soluble state. On the whole it may be stated that the oxidation state in which mercury will exist in nature depends on the redox potential and pH of the medium and on the nature of the anions and other chemical compounds with which it forms strong bonds.

The great stability of the Hg^{2+} ion in aqueous media is caused chiefly by two characteristics. The first is related to the fact that mercury characteristically forms covalent, not ionic, bonds. For this reason many of its compounds boil at low temperatures and dissolve in organic solvents better than in water. A second important property of this ion is its ability to form very stable complexes with many of the anions and compounds found in nature (Table 1).

Table 1. STABILITY CONSTANTS OF SEVERAL COMPLEXES OF DIVALENT MERCURY (2)

X	Cl^-	Bz^-	Y^-	NH_3	CN^-
K	10^{16}	10^{22}	10^{30}	10^{19}	10^{41}

$Hg^{2+} + 4X = HgX_4$; $K = [HgX_4]/[Hg^{2+}] \cdot [X]^4$

As a consequence, there is an almost total absence of free Hg^{2+} in seawater. Calculations based on the instability constants of the chemical state of metals have shown that their form in natural oxidizing waters can be controlled by a combination of pH and pCl. In seawater at a Cl^- concentration of 18.0 g/ℓ (pCl = 0.289) and pH 8, of the soluble compounds of divalent mercury, there are 92.4% of $HgCl_4^{2-}$, 6.3% of $HgCl_3^-$, 1.25% of $HgCl_2$, and less than 0.02% of Hg^{2+}, HgCl and $HgO \cdot H_2O$ taken together. Figure 1 is a diagram of the distribution for compounds of Hg^{2+} as a function of salinity at pH 8, provided that all of the $HgCl_2$ is dissolved in water (33).

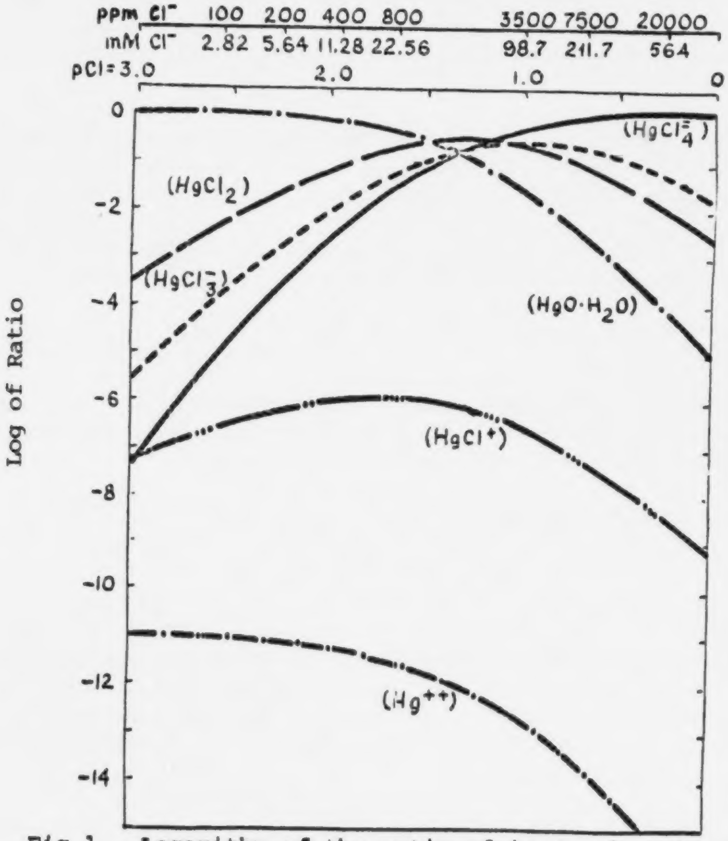


Fig 1. Logarithm of the ratio of inorganic mercury compounds to total mercury as a function of chloride ion concentration at pH 8 (33).

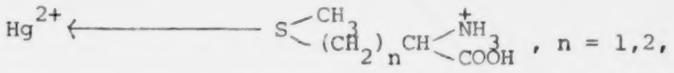
In the presence of sulfide ions, mercury precipitates as the very sparingly soluble sulfide HgS, which, however, in anaerobic seawater can go into solution by forming polysulfides; for example:

$$HgS_2^{2-} \xleftarrow{S^{2-}} HgS \xrightarrow{HS^-} HgS_2H^-$$

Under these conditions, free hydroxy and amino acids do not tie up metal ions (17).

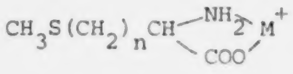
Mercury can form numerous complexes with products of decomposition and metabolism of marine organisms. On contact with the latter, it can react with their vitally important components, for example, proteins, nucleic acids, enzymes, etc., frequently with a fatal outcome for the organisms. The reaction centers in these types of compounds are mostly the sulfur, nitrogen, and oxygen atoms. Unfortunately, it is impossible to state the ligand (present together under different conditions and in different forms) mercury can react with to form more stable complexes because there is not enough factual information on their competitive reactivity and on their complexing ability with mercury. Nevertheless, some data apparently support this pattern. For example, a study of electron density transfer from ligands to mercury in complexes of the type $HgHal_2 \cdot XCH_2CH_2X$ (Hal = Cl, Br, I; X = Ome, SMe, NMe_2) by means of nuclear quadrupole resonance on halogen nuclei, which showed a decrease in the complexing capacity of these ligand atoms in the series $S > N > O$ (1).

The same conclusion is also supported by the study of the reaction of mercuric chloride with sulfur-containing α-amino acids in aqueous solution by means of proton magnetic resonance (pmr) spectra, which are strongly dependent on the pH (27). For example, while zinc and cadmium do not react with S-methlycycteine and methionine in acid solution, and mercury forms 1:2 complexes with localization of the bond on the sulfur atom

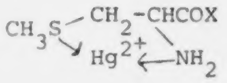


$$Hg^{2+} \longleftarrow S\begin{cases}CH_3\\(CH_2)_nCH\begin{cases}\overset{+}{N}H_3\\COOH\end{cases}\end{cases}, \ n = 1,2,$$

in alkaline solution all three cations form chelates of the composition 1:2 with coordination bonds M-O,N (I), except mercury reacting with S-methylcysteine to form a chelate (II) with Hg-S,N bonds



(I) M = Zn, Cd, Hg



(II)

The fact that mercury forms different types of complexes in alkaline solution is explained by the greater stability of the 5-membered Hg-O,N ring in comparison with the 6-membered Hg-S,N ring, i.e., the configurational and conformational stability of the complex as a whole is more important than the strength of the individual bonds.

An all important part in the binding of metal ions in seawater is played by organic carbon, which may be present in the dissolved state as well as in the form of colloidal and suspended particles. The latter are usually in the form of natural organic substances such as humic acids. The colloidal fraction of organic carbon usually is also classified as dissolved organic carbon, since it is not blocked by the filtering of natural water samples through a standard membrane filter with a pore diameter of 0.45 μ. The concentration of such combined "dissolved" organic carbon in seawater ranges from 0.3 to 2.0 mg/ℓ, (36), over 20% of it being in the form of colloidal particles 0.001 - 0.45 μ in size (32).

Depending on the pH of the water, the surface of the colloidal particles may be charged or neutral as a result of the dissociation or hydrolysis of the functional groups -OH, -SH, $-NH_2$, ^-NH and -COOH, which are the constituents of natural amino acids. The picture is complicated by the fact that, depending on the source, the organic colloids formed by the decay of plant and animal tissues may have changing properties and a changing number of different functional groups. The latter either generate a surface electrostatic charge that regulates surface adsorption or forms complexes. Thererfore, it is usually difficult to distinguish a metal species adsorbed on colloidal particles from a chemically bound species (32).

Organic matter can bind up to 60 per cent of dissolved mercury in coastal waters (15), and organic and inorganic colloidal particles can tie up most of the cadmium, lead, and copper (6). The lower the molecular mass of humic acids, the better they bind metals by complexing. Particularly effective in this respect are fractions with a mollecular mass up to 500 (28). The same behavior has been observed in the case of mercury (5). Nevertheless, it should be noted that other things being equal, the ability of organic matter to bind metals is strongly dependent on its origin.

Suspended particles of inorganic and organic origin usually bind metals by adsorption, not complexing, since their organic protion consists of substances of low oxidizing capacity that consequently have comparatively few functional groups. Therefore, when they reach seawater with the river runoff and industrial wastes, the heavy metal traces adsorbed on them pass into water as a result of complex formation. Up to 95 per cent of zinc and cadmium are thus desorbed (29).

In addition to forming a soluble mercury complex, soluble humic acids can reduce it to metallic mercury in accordance with a first-order kinetic equation at a fairly slow rate ($K = 0.009\ h^{-1}$) that depends only on the pH. According to Alberts et al. (14), the reaction mechanism consists in the action of three types of radical electrons of humic acid on Hg^{2+} (as demonstrated by esr spectra).

Turning to an examination of organic derivatives of mercury with an Hg-C bond (true organomercury compounds), one must note that only compounds of the type RHgX and R_2Hg (R - organic radical; X - organic or inorganic acid radical) can exist in the environment. It is interesting to note that similar compounds of cadmium and zinc are very easily decomposed by oxygen and water, and therefore cannot exist in nature. The greater the stability of organomercurials to water and air can be explained by the very low affinity of mercury for oxygen, not by a great stability of Hg-C bonds, which are fairly weak (the bond energy is 13-52 kcal/mole, depending on the radical). Nevertheless, under prolonged exposure to air, light, and heat, organomercuricals undergo an abiotic degradation in the environment; their reactivity is strongly dependent on the structure of the organic radical. Oxygen decomposes them in accordance with a free-radical mechanism to form intercalation and degradation products (21).

$$R_2Hg + O_2 \longrightarrow RHgOR$$

$$(C_nH_{2n+1})_2Hg + O_2 \longrightarrow C_nH_{2n+1}OH + C_nH_{2n}O + Hg^0$$

and ultraviolet (uv) light acts in accordance with the same mechanism, but leads to the formation of free radicals and mercury

$$R_2Hg \longrightarrow R^{\cdot} + RHg^{\cdot} \longrightarrow R^{\cdot} + Hg^0$$

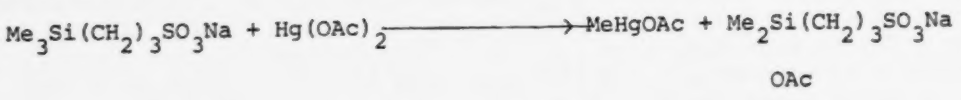
Of all the organomercury compounds in nature, a special role is played by derivatives of methylmercury because of its biological activity. Methylmercury causes chromosome damage (26) and is responsible for Minamata's disease. Organic compounds of mercury with other radicals have been studied very little, although their phenyl and butyl derivatives can be formed in nature as a result of human economic activity.

Among compounds of methylmercury, seawater contains 98 per cent MeHgCl, 2 per cent of MeHgOH, and practically no $MeHg^+$, as shown on a distribution curve for methylmercury compounds as a function of salinity at pH 8, providing that all of the MeHgCl is dissolved in water (Fig. 2) (33). This curve closely resembles that of the distribution of $HgCl_2$, except for the absence of complex ions.

Methylmercury in seawater can be formed chemically by irradiating mercuric acetate with uv light at 253.7 nm (or fluorescent light) (8).

$$Hg(OCOMe)_2 \longrightarrow MeHgOCOMe + Me_2Hg$$

or by exchange reactions with organosilicon, (11) organotin, and organolead compounds (8)



$$Me_3Si(CH_2)_3SO_3Na + Hg(OAc)_2 \longrightarrow MeHgOAc + Me_2\underset{OAc}{Si}(CH_2)_3SO_3Na$$

$$Me_3Sn^+ + Hg^{2+} \longrightarrow MeHg^+ + Me_2Sn^{2+}$$

Transfer of the methyl group from the silicon compound takes place quatitatively and, surprisingly, has not been known previously for nonaqueous solvents. The reaction with the tin derivative is described by a first-order kinetic equation with respect to each reactant and can obviously take place with other alkyl groupw as well, since it serves as a preparative method of obtaining alkylmercury halides in nonaqueous media.

The great affinity of mercury for sulfur accounts for the fact that even at very low concentrations of the alter in natural waters, over 99 per cent of methylmercury is bound in two sulfide compounds, $MeHgS^-$ and $(MeHg)_2$ at

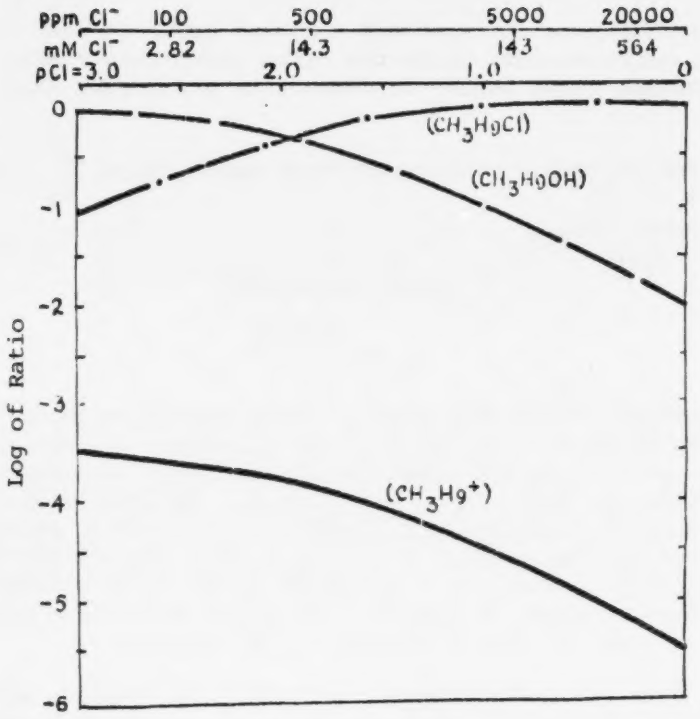


Fig 2. Logarithm of the ratio of methylmercury compounds to total methylmercury as a function of chloride ion concentration at pH 8 (33).

pH 5-9 (23). In addition, methylmercury can react with sulfide ions to form salts of tris(methylmercury) sulfonium (31), which is probably the most soluble and hence the most labile of the methylmercury derivatives present in the environment. It is in reversible equilibrium with the poorly soluble bis(methylmercury) sulfide ($K_{diss} = 10^{-7}$)

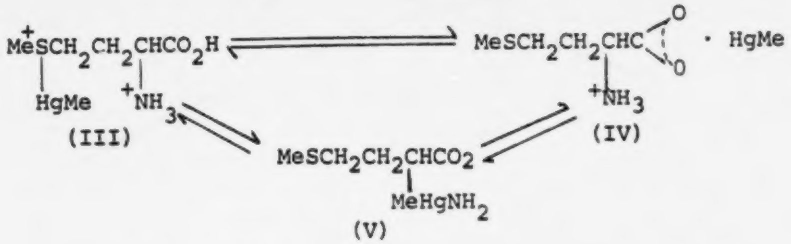
$$(MeHg)_3S^+ \rightleftharpoons (MeHg)_2S + MeHg^+$$

The stability of methylmercury in nature is also confirmed by the fact that in contrast to phenylmercury (10), the most active thiol-containing compounds do not split:

$$MeHgCl + RSH \longrightarrow MeHgSR$$

$$PhHgCl + RSH \longrightarrow RSHgCl$$

A very interesting property of methylmercury is the dependence of its reactivity in water on pH, as has been clearly demonstrated in the reaction with methionine (14). At pH < 2, methylmercury binds the thioester group into complex (III); starting at pH 2, it begins to move along the methionine molecule and probably reacts with the carboxyl group to form the compound (IV), and at pH 8-9, methylmercury binds the amino group into complex (V), which on further increase of pH begins to dissociate and breaks down completely at pH 13.5:



$\overset{+}{Me}SCH_2CH_2CHCO_2H$
HgMe
$^+NH_3$
(III)
$MeSCH_2CH_2CHCO_2 \cdot HgMe$
$^+NH_3$
(IV)
$MeSCH_2CH_2CHCO_2$
$MeHgNH_2$
(V)

The structure of the complexes has been demonstrated on the basis of the chemical shifts of protons in the CH_3^- and CH groups of mehtionine and methylmercury, as well as the constants of spin-spin interaction between the nuclei of mercury and hydrogen in esr spectra. The marked pH dependence of the complexing of methylmercury with methionine and other amino acids common in nature is due to the protonation of the ligand and the reaction of $MeHg^+$ with OH^-. The stability of these complexes at pH 7 and 9 decreases in the series sulfhydryl > amine > carboxyl > thioester when these groups are jointly present (Ref. 14 and references sited therein).

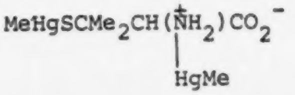
The structure of methylmercury complexes with α-amino acids has been confirmed by X-ray analysis. Methylmercury is bound to ℓ-cysteine via the sulfur atom

$$MgHgSCH_2CH(\overset{+}{N}H_3)CO_2^- \cdot H_2O,$$

and to d,ℓ-methionine, via the nitrogen with the structure of (V) (25), d,ℓ-Penicilamine reacting with mehtylmercury forms two 1:1 and 1:2 complexes (37, 38); in the 1:1 complex, the bond is formed via the sulfur atom

$$MeHg[SCMe_2CH(\overset{+}{N}H_3)CO_2^-] \cdot H_2O,$$

and in the 1:2 complex, via the sulfur and nitrogen atoms



$$MeHgSCMe_2CH(\overset{+}{N}H_2)CO_2^- \quad (N\text{—}HgMe)$$

Hence, α-amino acids are capable of binding two methylmercury groups. In all these complexes, a weak coordination bond is probably formed between the mercury atoms and the oxygen of the carboxyl group, the C-Hg-S fragment is almost linear, and the amino acids themselves are in the zwitter ion form. In contrast to Hg_2^+, which binds two amino groups, (see above), $MeHg^+$ binds only one, indicating its lower Lewis acidity.

One of the most important chemical properties of methylmercury is the reversible symmetrization reaction

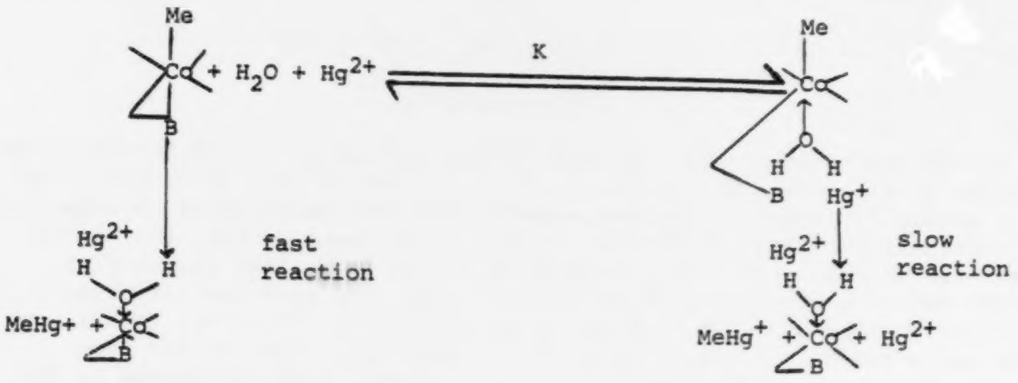
$$2MeHgX + 2L \longrightarrow Me_2Hg + HgX_2L_2$$

The role of symmetrizing agents L is to effectively bind the inorganic mercury salt by complexing, precipitation, or reduction in order to shift the equilibrium to the right. In nature, such agents can be cyanides, iodides, amines, and phosphines. Alumina is also active. However, precipitation materials and sulfur-containing compounds are not. Therefore, Me_2Hg in nature is chiefly formed via methylcobalamin (10), and this promotes its fairly good solubility in seawater (2.1 g/kg) (35).

In nature, methylmercury derivatives can be formed not only chemically but also biochemically; the latter mode is the object of the most serious study at the present time. The majority of researchers believe that methylmercury is the cause of poisoning of numerous aquatic organisms since it has been found in tissues bound to sulfhydryl groups of proteins. Its great toxicity in comparison with metallic or inorganic mercury is explained by a solubility that is two orders of magnitude greater in fats than in water, thus considerably facilitating its penetration into cells.

It was shown previously that Hg^{2+} is methylated by methpentacyanocobaltate prepared as a model of vitamin B12 (18). Subsequently, it was found that this reaction takes place in natural systems (19, 40) in the presence of only those microorganisms whose enzyme studies contain the coenzyme methylcobalamin, the methylated form of vitamin B12. This is explained by the fact that of all the known methylating reactants present in biological systems, only methyl-B12, which belongs to the class of methylcorrinoids, is able to transfer the methyl group in the form of an anion, i.e., CH_3^- (20, 22, 39). The mechanism of this reaction consists in an electrophilic attack on the methyl anion by the mercury ion and is common in the chemistry of organomercury compounds.

A study of the reaction kinetics showed that the rate of transfer of methyl anion depends on the equilibrium constant K, the slow reaction being 1000 times slower than the fast reaction. Dimethylmercury is formed similarly, but only from $MeHg^+$, at a rate 6000 times slower than the rate of synthesis of methylmercury (Bz-5,6-dimethylbenzimidazole) (34, 39):



Microbial methylation can occur under aerobic as well as anaerobic conditions (7). It is proportional to the rate of growth and metabolic activity of the methylating microorganisms, temperature, concentration of mercury ions, their accessibility, and presence of organic matter. The optimum concentration of the latter is estimated from the biochemical oxygen demand and equal to 8 mg/ℓ or more (33). Methylation takes place best at pH 4.5. Certain bacteria form methylmercury from phenylmercury, and with greater ease than from inorganic mercury (13).

The biochemical methylation of mercury occurring under natural conditions may present a serious threat in the inland and coastal waters where mercury is discharged with waste waters. Locations have already been identified where the mercury thus dumped and held by silting deposits is methylated in a few years instead of a few centuries (9). This disrupts the natural equilibrium and leads to the concentration of mercury in aquatic organisms such as mollusks, seaweed, and fish, whose consumption by man may lead to serious poisoning. Waste waters also pose another danger in that by supplying methylcobalamin-containing nutrients to microorganisms, they promote their multiplication and help to maintain anerobic conditions which protect methylcobalamin from irreversible photochemical breakdown in the presence of oxygen. Attempts to prevent the biosynthesis of methylmercury unfortunately have proven unsuccessful. For example, the binding of inorganic mercury into mercury sulfide merely leads to a decrease in the reaction rate by several orders of magnitude (12).

The ability of certain microorganisms to mineralize methylmercury to metallic mercury and methane (24) unfortunately cannot prevent the accumulation of mercury in aquatic organisms because the rate of formation of methylmercury in nature exceeds the rates of its decomposition.

The formation and decomposition of methylmercury are not the only natural biological processes in the transformation of mercury. Thus, the enzymes present in many bacteria reduce divalent mercury to the metallic state; the reduction of nicotinamide adenine dinucleotide (NADH) is used as a coenzyme for catalysis, and certain microorganisms oxidize mercury sulfide to the sulfate, causing the mercury in the latter case to go into solution (see the reference in 39):

$$Hg^{2+} + NADH + H^{+} \rightleftharpoons Hg^{0} + 2H^{+} + NAD^{+}$$

$$HgS \longrightarrow HgSO_4.$$

Ignoring the metal species leads to serious errors in the determination of their total content in seawater. It is well-known that the majority of heavy metals in aqueous media are adsorbed and chemically bound to organic and inorganic colloidal particles. It has always been assumed that heavy metals can be quantitatively concentrated either by passing the samples through cation exchange resins or by complexing them with various organic compounds, mainly chelates, and by liquid extraction. However, it has been shown quite recently by means of radioisotopes that resins of the type "Chelex-100," most widely used abroad (in the USSR, their prototype is the KU-2 resin), block only the dissolved and labile inorganic species of zinc, cadmium, lead, and copper, and allow the ions of these metals bonded to colloidal particles to pass through. This is because in most cases the dimensions of the latter are too large to permit them to enter the pores of the high molecular resin molecules where the cation exchange takes place.

A similar situation is observed in the case of the most frequently employed extraction of heavy metals by means of ammonium pyrrolidinedithiocarbamate in methyl isobutyl ketone at pH 4.5. Under these conditions, only copper is completely extracted, while lead and zinc are extracted only to the extent of 35-65 and 23-59%, respectively. The extraction with chelate in comparison with resin is more effective only because organic colloids dissolve in the ketone. To achieve a complete separation of heavy metals from colloidal particles, the latter must be broken up. The breakup is accomplished by boiling the samples in strongly acidic solutions at pH 0.7, then alkalizing to pH 4.5-8.1 and concentrating either on a resin or by complexing (16). This behavior will also undoubtedly apply to mercury, although the latter was not considered in the study.

It was also found that among minerals containing organic matter and sulfur compounds, mercury for analysis can be quantitatively separated only by treating the samples with aqua regia or with oxidizing mixtures containing chloride ion (3). This would also undoubtedly apply to samples of seawater and bottom sediments as well.

Researchers have determined the total content of mercury (and other heavy metals) in objects in the environment with indefinitely low results (3 and 16). Their studies should apparently lead to a serious revision of the concepts based on the reliability and accuracy of methods of quantitative determination of heavy metals in objects in the environment, for example, the calculation of their balance.

REFERENCES

1. Bryukhova, Ye. V., N. S. Erdyneyev, and A. K. Prokof'yev. 1973. NQR Spectra of ^{35}Cl, ^{79}Br, ^{81}Br, and ^{127}I of the Complexes $HgHaI_2.XCH_2CH_2X$, X= OMe, SMe, NMe_2. Izvestiya AN SSSR, ser. khim., No. 8, pp. 1895-1897.

2. Cotton, F., and D. Wilkinson. 1969. Modern Inorganic Chemistry, Part II. Mir, Moscow, pp. 464-487.

3. Agemain, H., and A.S.Y. Chau. 1976. An Improved Digestion Method for the Extraction of Mercury from Environmental Samples. Analyst, Vol. IOI, No. 2, p. 91-95.

4. Alberts, J.J., J.E. Schindler, and R.W. Miller. 1974. Elemental Mercury Evolution Mediated by Humic Acid. Science, 1974, Vol. 184, No. 4139, p. 895-897.

5. Andren, A.W. and R.C. Harriss. 1975. Observations on the Association between Mercury and Organic Matter Dissolved in Natural Waters. Geochim. Cosmochim. Acta Vol. 39, No. 9, p. 1253-1257.

6. Batley, G.E., and T.M. Florence. 1976. Determination of the Chemical Forms of Dissolved Cadmium, Lead, and Copper in Seawater. Marine Chemistry, Vol. 4, No. 4, p. 347-363.

7. Bisogni, J.J., and A.W. Lawrence. 1975. Kinetics of Mercury Methylathion in Aerobic and Anaerobic Aquatic Environments. J. Water Pollut. Control Fed., Vol. 47, No. 1, p. 135-152.

8. Coyle, T.D., K.L. Jewett, and F.E. Brincman. 1975. Formation and Reactivity of Organometals in Aqueous Media. Seventh Inter. Conf. on Organometallic Chemistry. Venice, Italy. Abstract No. 106.

9. Cross, R.J. 1973. Organomercurials in the Environment. Chem. Ind. No. 15, p. 719-721.

10. Cross, R.J., and C.M. Jenkins. 1975. Chemical Studies Relating to Environmental Organomercuricals. Environ. Pollut. Vol. 8, p. 179-184.

11. DeSimone, R.E. 1972. Methylation of Mecury by Common Nuclear Magnetic Resonance Reference Compounds. Chem. Commun. No. 13, p. 780-781.

12. Fagerstrom T., and A. Jernelov. 1971. Formation of Methylmercury from Pure Mercuric Sulphide in Aerobic Organic Sediment. Water Res. Vol. 5, No. 3, p. 121-122.

13. Fagerstrom, T., and A. Jernelov. 1972. Some Aspects of the Quantitative Ecology of Mercury. Water Res. Vol. 6, No. 10, p. 1193-1202.

14. Fairhurst, M.T., and D.L. Rabenstein. 1975. Nuclear Magnetic Resonance Studies of the Solution Chemistry of Metal Complexes. XII. Binding of Methylmercury by Methionine Inorg. Chem. Vol. 14, No. 6, p. 1413-1415.

15. Fitzerald, W.F., and W.B. Lyons. 1973. Organic Mercury Compounds in Coastal Waters. Nature (London), Vol. 242, No. 5398, p. 452-453.

16. Florence, T.M., and G.E. Batley. 1976. Trace Metal Species in Seawater I. Removal of Trace metals from Seawater by a Chelating Resin. Talanta, Vol. 23, No. 3, p. 179-186.

17. Gardner, L.R. 1974. Organic Versus Inorganic Trace Metal Complexes in Sulfidic Marine Water--Some Speculative Calculations Based on Available Stability Constants. Geochim. Cosmochim. Acta. Vol. 38, p. 1297-1302.

18. Halpern, J., and J.P. Maher. 1964. Pentacyanobenzycobaltate (III). A New Series of Stable Organocobalt Compounds. J. Amer. Chem. Soc. Vol. 90. No. II, p. 2311.

19. Jensen, S., and A. Jernelov. 1969. Biological Methylation of Mercury in Aquatic Organisms. Nature (London), Vol. 223, No. 5207, p. 753-754.

20. Hill, H.A.O., J.M. Pratt, S. Ridsdale, F.R. Williams, and R.J.P. Williams. 1970. Kinetics of Substitution of Co-coordinated Carbanions in Cobalt (III) Corrinoids. Chem. Commun. No. 6, p. 341.

21. Markarova, L.G. 1971. Reactions of Organomercury Compounds, Part 2. In: Becker, E.I., Tsutsui, M. (Eds). Organometallic Reaction. Vol. 2. Wiley Publishing Co., New York, p. 335-421.

22. Agnes, G., S. Bendle, H.A.O. Hill, F.R. Williams, and R.J.P. Williams. 1971. Methylation by Methyl Vitamin B12. Chem. Commun., No. 15, p. 850-851.

23. Zepp, R.G., G.L. Banghman, N. Lee Wolfe, and D.M. Cline. 1974. Methylmercuric Complexes in Aquatic System. Environ. Letters, Vol. 6, No. 2, p. 117-127.

24. Spangler, W.J., J.L. Spigarelli, J.M. Rose, and H.M. Miller. 1973. Methylmercury: Bacterial Degradation in Lake Sediments. Science, Vol. 180, No. 4082, p. 192-193.

25. Wong, Y.S., N.J. Taylor, P.C. Cnieh, and A.J. Carty. 1974. Models for the Methylmercury-protein Interaction: A Comparison of the Molecular Structures of Methyl-ℓ-Cysteinatomercury (II) and Methyl-d,ℓ-methioninemercury (II). Chem. Commun. No. 15, p. 625-626.

26. Mulvihill, J.J. 1972. Congenital and Genetic Diseases in Domestic Animals. Science. Vol. 176, No. 4031, p. 132-137.

27. Natusch, D.F.S., and L.J. Porter. 1971. Proton Magnetic Resonance Studies of Metal Complex Formation in Some Sulfur-containing α-Amino acids. J. Chem. Soc. (A), No. 16, p. 2527-2535.

28. Rashid, M.A. 1971. Role of Humic Acis of Marine Origin and Their Different Molecular Weight Fractions Complexing Di- and Tri-valent Metals. Soil Sci. Vol. III, p. 298-306.

29. Rohatgi, N. and K.Y. Chen. 1975. Transport of Trace Metals by Suspended Particulates on Mixing with Seawater. J. Water Pollut. Control. Fed. Vol. 9, p. 2298-3016.

30. Sanemasa, I. 1975. The Solubility of Elemental Mercury Vapor in Water. Bull. Chem. Soc. Japan, Vol. 48, No. 6, p. 1795-1798.

31. Schwarzenbach, G. and M. Schellenberg. 1965. Komplexchemie de Methylquecksilber-kations. Helv. Chim. Acta, Vol. 48, No. I, p. 28-46.

32. Sharp, J.H. 1973. Size Classes of Organic Carbon in Seawater. Linmol. Oceanogr. Vol. 17, p. 494-498.

33. Shin, E.B. and P.A. Krenkel. 1976. Mercury Uptake by Fish and Biomethylation Mechanisms. J. Water Poll. Control Fed. Vol. 48, No. 3, p. 473-501.

34. DeSimone, R.E., M.W. Penley, L. Charbonneau, S. Smith, J.M. Wood, H.A.O. Bill, P. Ridsdale, and R.J.P. Williams. 1973. The Kinetics and Mechanisms of Cobalmin-dependent Methyl and Ethyl Transfer to Mercuric Ion. Biochem. Biophys. Acta., Vol. 304, p. 851-863.

35. Wasik, S.P., R.L. Brown, and J.I. Minor. 1976. Partition Coefficients and Solubility Measurements of Dimethylmercury in Fresh and Seawater over a Temperature Range 0-25°C. J. Environ. Sci. Health - Environ. Sci. Eng. Vol. All, No. I, p. 99-105.

36. Williams, P.M. 1971. The Distribution and Cycling of Organic Matter in the Ocean. In: S.J. Faust, J.V. Hunter (Eds). Organic Compounds in Aquatic Environments. Marcel Dekker, New York, p. 145-163.

37. Wong, Y.S., P.C. Chieh, and A.J. Carty. Binding of Methylmercury by Amino-acids: X-ray structure of D,ℓ-penicilaminatomethylmercury (II). Chem. Commun., No. 19, p. 741-742.

38. Wong, Y.S., P.C. Chieh, and A.J. Carty. 1973. The Interaction of Organomercury pollutant with Biologically Important Sites: an X-ray Study of the 2:1 Complex between Methylmercury and Penicilamine. Can. J. Chem. Vol. 51, No. 15, p. 2597-2599.

39. Wood, J.M. 1974. Biological Cycles for Toxic Elements in the Environment. Science. Vol. 183, No. 4129, p. 1049-1052.

40. Wood, J.M., F.S. Kennedy, and C.G. Rosen. 1968. Synthesis of Methylmercury Compounds by extracts of Methanogenic Bacterium. Nature (London), Vol. 220, No. 5163, p. 173-174.

THE FATE OF HEAVY METALS ADDED TO THE GULF OF MEXICO BY THE MISSISSIPPI RIVER

B. J. Presley and J. H. Trefry
Department of Oceanography, Texas A&M University
College Station, Texas 77843

Anthropogenic heavy metals, along with other materials, may be transported to the ocean from continents by atmospheric processes, direct dumping, sewage outfalls, storm runoff, and river and ground-water discharge. The relative importance of these pathways for most substances is not well known. However, there is general agreement with the suggestion of Dyrssen et al. (4) that atmospheric transport may be mainly responsible for addition of pollutants to the open sea, whereas the other routes are probably more important to coastal waters. River discharge is certainly dominant in total transport. Garrels and MacKenzie (9) estimate that rivers carry 90 per cent of the total dissolved and suspended solids that are added to the oceans. Rivers also carry domestic and industrial wastes away from most major communities, and thus must be responsible for much of the man-derived substances added to the ocean.

The major U.S. river is the Mississippi which drains 41 per cent of the conterminous U.S. Its drainage basin stretches from New York to Montana and from Canada to the Gulf of Mexico (Fig. 1). The Mississippi is estimated to carry about 60 per cent of the total dissolved solids (16) and 66 per cent of the total suspended solids (3) transported to the oceans from the conterminous U.S. Estimates of industrial, municipal, and agricultural waste inputs into the Mississippi River (8) suggest that the river pollutant load is large and diverse. For example, recent data show that river phenol concentrations consistently exceed public water supply criteria (25) and that the river has a significant anthropogenic contribution of light carbons (2) and phthalic acid esters, DDTs, and PCBs (10). Added to this load is the domestic sewage from almost 2 million people in the lower Mississippi area alone. In addition to organic substances, an estimated 18 million kilograms of inorganic wastes also discharged into the lower Mississippi River daily (8). This flux is equivalent to 7 per cent of the total dissolved load at average river flow and 21 per cent of the total at low flow. Little data are available on the chemical composition of this industrial discharge; however, such wastes are known to contain various heavy metals (19).

The work presented here characterizes and quantifies the particulate and dissolved metal load of the Mississippi River and examines metal distribution in Mississippi Delta suspended matter, plankton, and sediments. The overall objectives of this work are to assess the magnitude of any anthropogenic metal contribution by the Mississippi River and to determine its fate in the Gulf of Mexico.

Reproduced from
best available copy.

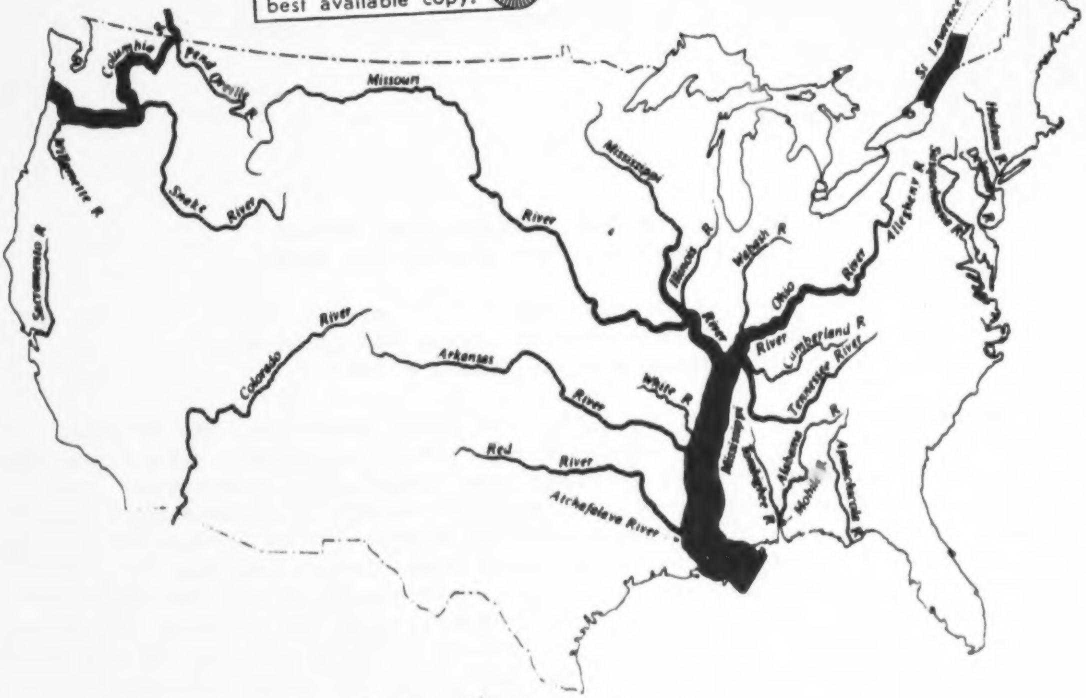


Figure 1. Large rivers in the United States (15).

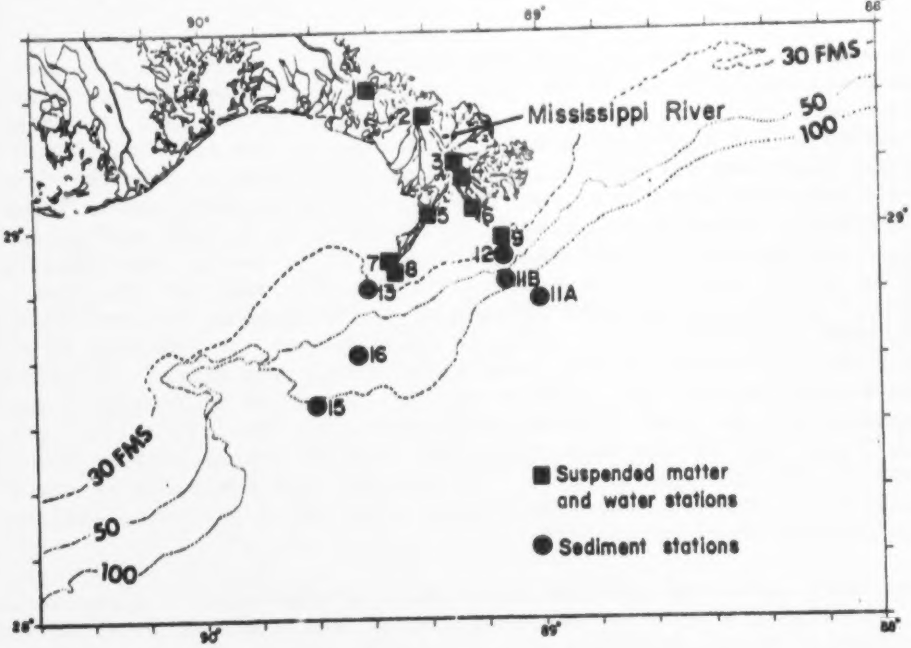


Figure 2. Mississippi River and Delta water, suspended matter, and sediment sampling sites.

Mississippi River dissolved metal concentrations from locations shown in Fig. 2 were found to be low and, with the exception of Zn, are considerably below those established for water quality criteria (Table 1). The dissolved fraction accounts for <10 per cent of the total river metal load for most metals studied (Table 2). This is most likely due to the adsorption of metal species on the abundant river suspended matter (>300mg/ℓ) at the relatively high river pH (7.5 to 8.0).

River particulate metal concentrations (Table 1) were constant during four sampling periods when the river was at average and above average flow. During low flow, an increase in particulate organic matter concentrations (from <3 to 25 per cent) brought about a corresponding decrease in Fe and Al concentrations due to dilution of alumino-silicate detritus and a 30 to 40 per cent increase in Mn, Zn, and Cu concentrations due to an association of these metals with the increased organic matter. Of the metals studied, only Zn was found in concentrations higher than those accepted as suitable for dredged sediment disposal. Dumping criteria based on bulk chemistry ignore the geochemical form of the metal and do not necessarily predict the biological availability of excess metal loads, but point out unusual concentrations indicative of man-introduced material. Three metals (Zn, Pb, and Cd) were found to be in much higher concentrations in the river particulates than in average continental crust (Table 1).

Physio-chemical interactions involving heavy metals, reportedly occurring across the freshwater/seawater interface, may affect both the ultimate area of metal deposition and their availability to nearshore marine organisms. Desorptive processes would make metals more available to organisms and delay their removal to the sediments, whereas adsorptive processes would have an opposite effect. Comparison of our suspended matter data from the Mississippi River with that in saline waters from immediately outside the river mouth (Table 1) shows that (with the exception of Cu and Zn) concentrations are essentially the same. These observations argue against extensive desorption of any of these metals and suggest that Cu and Zn levels actually increase in particulates from salt water, perhaps due to the increased percentage of organic carbon.

It has long been known that marine plankton greatly concentrate certain trace elements from seawater (26, 11). There has also been considerable speculation on the importance of plankton in transporting trace elements from surface to deep water or from water to sediments (12, 1). Thus, plankton are potentially a key factor in removing pollutant metals from seawater.

Phytoplankton collected from the Mississippi Delta area and the northwest Gulf of Mexico (Fig. 3) had quite variable trace metal concentrations, but similar values and variability have been reported in other studies (14, 17).

Previous works have found little correlation between trace metal concentrations and the species composition of phytoplankton samples, and that generalization holds for the Gulf of Mexico samples. There seems, however, to be an indication of Pb enrichment in samples from near the river mouth. For example, samples 8, 9, and 11 (Table 3), which were collected on the same day,

TABLE 1. MISSISSIPPI RIVER DISSOLVED AND PARTICULATE METAL CONCENTRATIONS AND ENVIRONMENTAL QUALITY CRITERIA

Dissolved metal concentrations in μg/ℓ

	Fe	Mn	Zn	Pb	Cu	Ni	Cr	Cd	Hg
Mississippi River (N=10)	10	10	10	1	2	1	0.5	0.1	0.5
Water quality criteria (EPA, 1973)	300	50	1	30	60	100	50	4	2
Ave. river water (Turekian, 1974)	-	7	20	3	7	0.3	1	-	0.07

Particulate metal concentrations in μg/ℓ

	Fe	Mn	Zn	Pb	Cu	Ni	Cr	Cd	Co
Mississippi River (N=34)	46,100	1,300	193	45	45	55	80	1.3	21
Mississippi Delta (N=34)	46,400	1,290	244	49	56	56	84	1.5	21
Sediment disposal criteria (EPA, 1973)	-	-	75	50	50	-	-	2	-
Ave. crustal abundance (Taylor, 1961)	56,300	950	70	13	55	75	100	0.2	25

TABLE 2. ANNUAL FLUX OF METALS FROM THE MISSISSIPPI RIVER TO THE GULF OF MEXICO*

Element	Particulate (x 10^9g)	Dissolved (x 10^9g)	Particulate (% of total)	Dissolved (% of total)
Fe	12,900	5.7	99.9	0.02
Mn	364	5.7	98.5	1.5
Zn	54	5.7	90.4	9.6
Cr	22	0.3	98.7	1.3
Ni	16	0.6	96.4	3.6
Cu	13	1.1	92.2	7.8
Pb	13	0.3	97.7	2.3
As	4	0.6	87.0	13.0
Cd	0.4	0.06	87.0	13.0

*Calculations are based on average water and suspended matter data from Table 1 with the sediment discharge data of the U.S. Army Corps of Engineers (2.8 x 10^{14}g/y; 1950-1974) and estimated water flow at the river mouths (5.7 x 10^{14}ℓ/y; Iseri and Langbein, 1974).

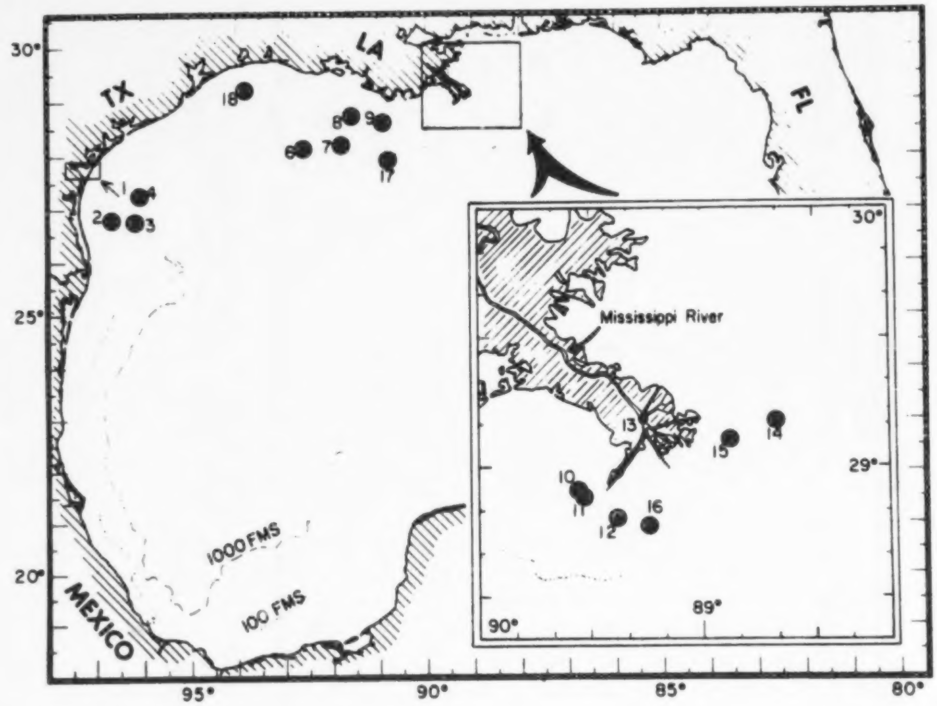


Figure 3. Location of plankton sites in the northwest Gulf of Mexico and the Mississippi Delta.

show a three-fold decrease in Pb to Al ratio in moving away from the river. The pattern of Pb concentration around the river mouth can be complicated by various factors. For example, sample 10 (taken near the river mouth during an intense plankton "bloom") does not show high Pb, but sample 12 (from outside the "bloom") does. The overall average Pb concentration of these northwest Gulf of Mexico samples is also higher than values reported by Martin and Knauer (17) from Monterey Bay, also suggesting Pb contamination in some nearshore phytoplankton.

Zooplankton trace metal concentrations show no pattern that would indicate an adverse effect from the Mississippi River (Table 4), but, as with phytoplankton, it is necessary to consider some of the factors that can complicate the gross distribution pattern. Three samples collected offshore from Corpus Christi were enriched in Pb, Cd, and Cu, compared to samples from the immediate Mississippi River Delta area and those from offshore Louisiana. The samples from Corpus Christi were predominantly copepods (unlike most of the other samples) but does not explain all of their metal enrichment because one sample from near the Mississippi River had a high copepod component, but low trace metals. Likewise, clay contamination can explain some, but not all of the enrichment. Data on 74 additional zooplankton samples from South Texas analyzed in our laboratory (13 and unpublished data) show large variations in most trace metals, but generally higher Pb, Cd, and Cu concentrations than in

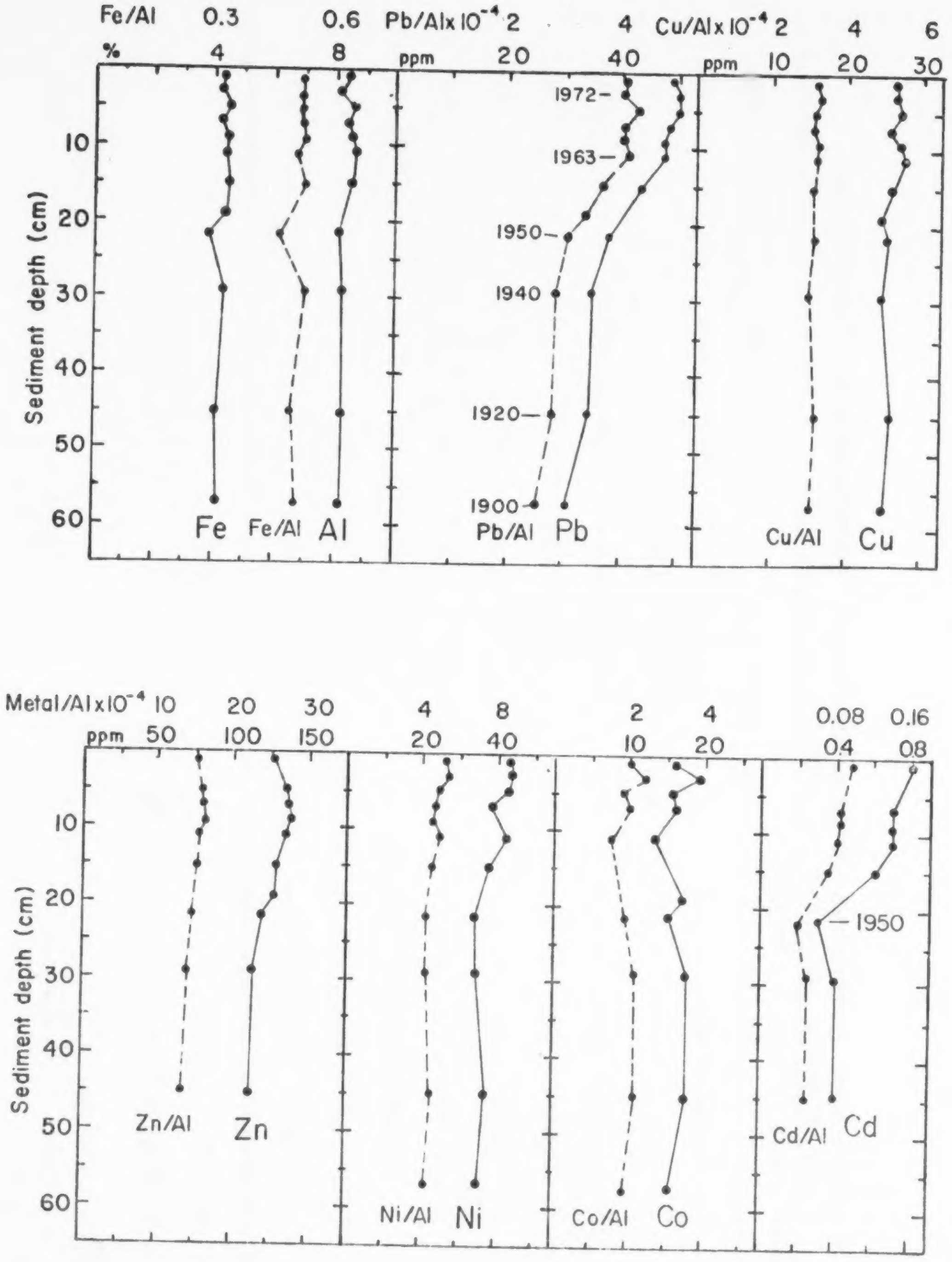


Figure 4. Vertical metal profiles for Station 16 sediment (water depth 110m). Dates based on Pb-210 geochronologies (20).

TABLE 3. HEAVY METAL DISTRIBUTION IN SARGASSUM AND MIXED PHYTOPLANKTON FROM THE NORTHWEST GULF OF MEXICO AND MISSISSIPPI DELTA

(Concentrations in μg/g Dry Weight)

Location	Al	As	Cd	Co	Cu	Fe	Pb	Mn	Ni	Zn
1[a]	13,450	5.1	1.1	4.0	6.2	7,550	20.1	181	7.9	40
8	6,431	47.0	1.8	4.0	11.0	3,514	12.9	77.2	4.8	74
9	6,396	52.0	1.5	6.6	25.2	5,886	21.3	135	1.1	129
0	1,072	5.5	4.3	< 0.5	5.1	1,094	5.8	19.4	0.9	55
1	3,036	-	0.2	1.0	6.6	2,887	29.0	115	4.8	22
2	3,894	-	1.4	2.5	6.0	3,115	13.7	80.9	11.0	52
4	1,364	2.9	<0.05	1.8	1.2	1,277	2.5	21.2	4.5	13
7[b]	33	82.0	1.7	0.9	5.1	61	9.1	4.5	15.6	34
8[b]	903	40.0	4.6	4.1	10.6	685	39.2	21.4	2.6	87

Source: Sims, 1975

[a] Median of 10 samples from Corpus Christi Bay

[b] Sargassum

TABLE 4. HEAVY METAL DISTRIBUTION IN MIXED ZOOPLANKTON FROM THE NORTHWEST GULF OF MEXICO AND THE MISSISSIPPI DELTA

(Concentrations in μg/g dry weight)

Location	Al	As	Cd	Co	Cu	Fe	Pb	Mn	Ni	Zn
2	1,252	7.6	2.4	0.9	74.0	799	15.3	12.6	2.0	155
3	4,266	6.9	4.4	1.5	23.1	3,663	62.5	105	6.1	200
4	500	7.3	4.4	2.0	25.6	977	16.5	21.8	2.9	133
6	75	-	2.9	2.1	8.9	77	8.5	7.5	7.8	135
7	103	5.8	1.9	< 0.5	7.5	122	1.2	13.7	2.8	86
8	340	12.0	1.5	< 0.5	8.2	305	2.3	9.2	2.7	75
9	225	4.9	1.0	< 0.5	4.3	270	6.2	10.3	1.0	41
10	314	1.9	2.9	< 0.5	6.1	397	2.5	16.3	1.4	139
11	266	9.0	0.9	< 0.5	8.6	300	< 0.5	8.4	8.2	107
12	426	3.9	2.4	1.1	6.5	532	< 0.5	28.0	3.5	116
14	6,000	6.5	1.2	< 0.5	3.5	4,035	5.1	114	7.4	52
15	4,620	6.4	2.6	0.8	6.6	4,760	8.3	70.4	6.6	68
16	51	23.1	0.4	< 0.5	35.3	62	3.0	4.7	< 0.5	49
17	44	29.5	2.5	0.7	9.2	237	7.4	7.7	1.4	57

Source: Sims, 1975

the Mississippi River Delta samples. Further, the values are not greatly different from values given by Martin and Knauer (17). Thus the river does not appear to grossly contaminate zooplankton, but taxonomy as well as location must be considered before a judgment can be made.

Productivity in the delta area is high (450g C/cm^2/yr) (El-Sayed, personal communication), but the distribution of species, grazing rate, and fate of the produced carbon are not well known. In the open sea, most organic carbon is destroyed before it is buried in the sediments (18, and references therein). Such destruction also seems to be true here (despite the shallow water), because our unpublished data from more than 20 cores in the area show the organic carbon content of the sediments (∿0.5% organic C) to be similar to that of the river-suspended matter. Low organic C would be expected near and to the west of the delta even if all of it survived to be buried. The detrital sediment there is accumulating at rates of 5 g/cm^2/yr or faster, and effectively dilutes the 0.045gC/cm^2/yr being produced. The sedimentation rate drops very rapidly to 0.5g/cm^2/yr or less outside the 100m isobath and to the east of the delta; yet the organic carbon percentage in the sediments goes up only slightly. Obviously, little of the carbon is being buried. By similar reasoning, plankton are responsible for little trace metal enrichment of the sediments. These sediments are relatively constant in composition over an area of measured or implied high variation in detrital sedimentation rate.

Nearshore sediments provide both the major sink for the riverine metal flux and a historical record of metal input. To trace the history of metal input to the Mississippi Delta the Pb^{210}, we applied dating method to some of the cores (20), thus allowing dates to be assigned to the vertical sediment metal profiles. Metal concentrations are shown normalized to Al to correct for changes in CaCO$_3$, salt content, and mineralogy. This can also be done by normalizing to Fe as demonstrated by Trefry and Presley (23).

Fig. 4 for mid-delta station 16 (Fig. 2) shows that there has been a relatively homogeneous flux of Fe, Al, Cu, Zn, Ni, and Co to these sediments over the past 75 years. Pb concentrations, however, have increased by 65 per cent during this time interval, the major onset occurring since the mid-1940's (a period of increased usage of leaded gasoline). Surface sediment Pb concentrations (∿45ppm, salt-free, CaCO$_2$-free) at Station 16 are comparable to those of present-day river particulates (46ppm). In addtion to Pb, surface sediment Cd concentrations are also high, (double their pre-1950 values). Moreover, the 1950 0.4ppm Cd baseline concentration is still in excess of values found in deeper sediments from the delta. Mid-delta Stations 14 and 11B (Fig. 2) had metal distribution similar to that in Station 16.

Rapidly accumulating sediments (>3g/cm^2-y) near the river mouth area of the delta also have relatively straight vertical metal profiles (Fig. 5). However, Pb and Cd concentrations, 70 and 200 per cent, respectively, above base values found at Station 16, are in good agreement with river particulate concentrations. Uniform Pb and Cd concentrations of 40ppm and 1ppm, respectively, for 50- to 60-cm profiles in this area can only indicate that the pollutant levels have been relatively constant during the past 10 to 15 years.

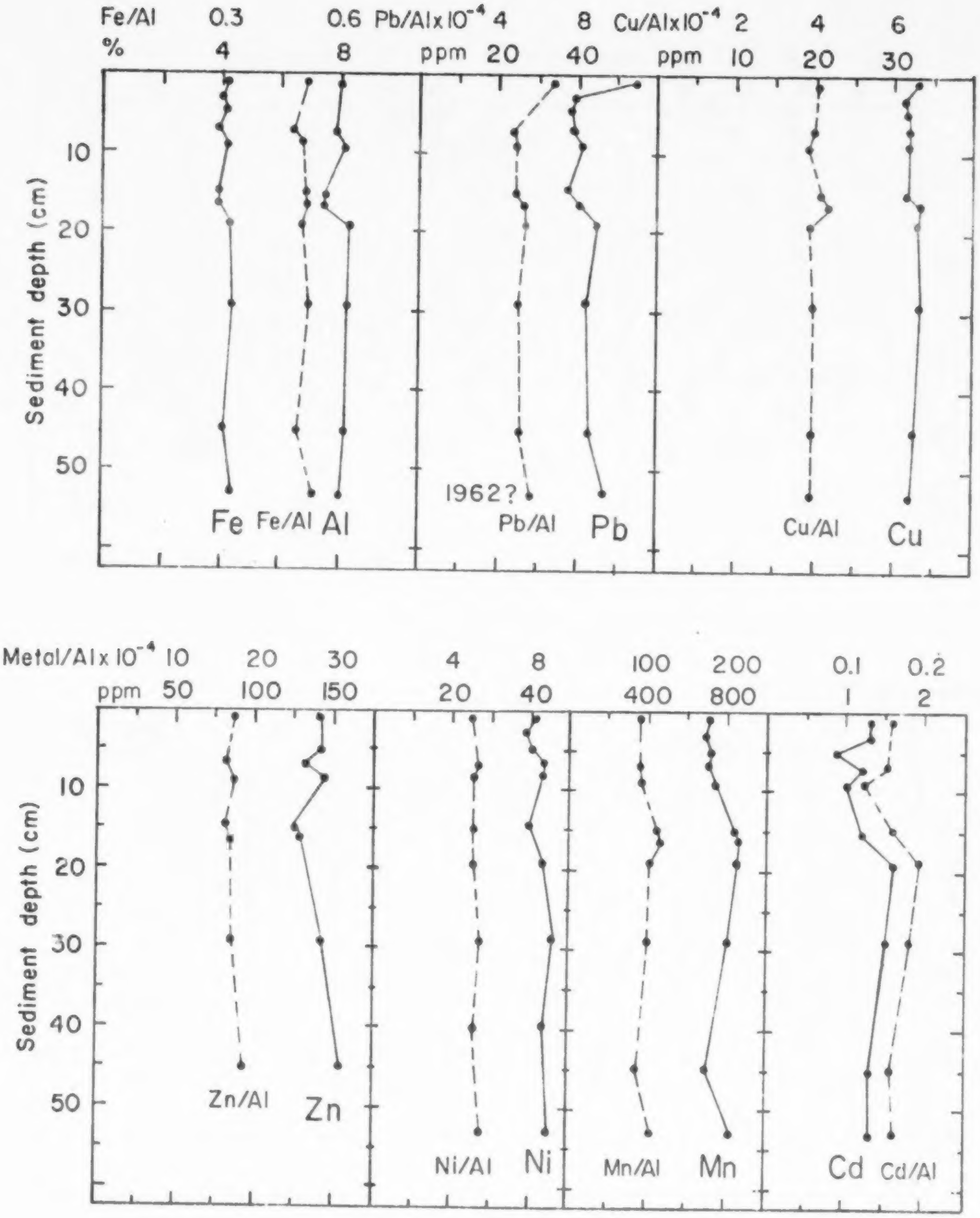


Figure 5. Vertical metal profiles for Station 9 sediment (water depth 50m).

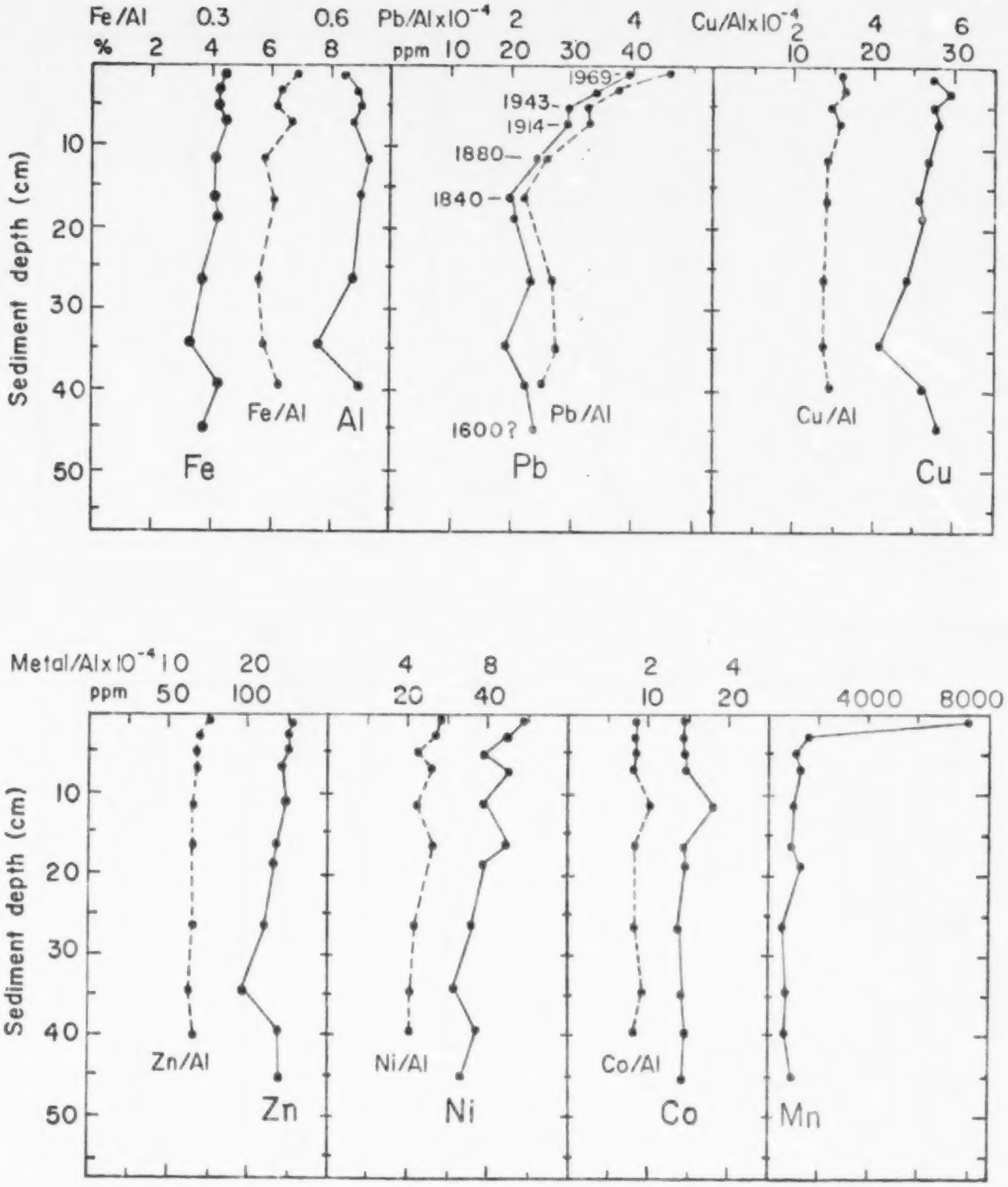


Figure 6. Vertical metal profiles for Station 15 sediment (water depth 550m). Dates based on Pb-210 geochronologies (20).

Outer delta sediments from Station 15 and Station 11A (Fig. 2), where accumulation rates are on the order of 0.1 g/cm^2-y, also have relatively constant Fe, Al, Cu, Zn, Ni, and Co concentrations, or at least uniform metal/Al ratios (Fig. 6). High surface Mn concentrations result from a geochemical redistribution of Mn in the sediment column, rather than a time-dependent supply. Pb concentrations at Station 15 (Fig. 6) decrease from 43ppm (salt-free, $CaCO_3$-free) at the surface to 20 to 25ppm in the lower core section. The time scale for this sample, however, permits an extension of the historical record which shows the onset of pollutant Pb to have occurred about 1840. This initial flux is followed by the previously observed period of increase during the mid-1940's and is consistent with Pb profiles for Lake Michigan sediments presented by Edgington and Robbins (5) who attribute excess Pb deposited prior to 1920 to inputs from the combustion of coal.

Despite the uniformity of Cu, Ni, and Mn profiles in nearshore sediments, the absolute values (and metal/Al ratios) are 20 to 40 per cent lower than those for river particulates. Interstitial water Mn gradients support losses of Mn to the overlying seawater by reduction-diffusion. We do not have pore water data for the other metals, but merely point out the possibility that some of the metal deposited in rapidly accumulating, anaerobic sediment may be subsequently returned to the overlying water or the surface-most layers of sediment. This would increase, of course, the availability of these metals to the benthic community.

In summary, we find very low levels of dissolved trace metals in Mississippi River water and no evidence of Fe, Mn, Cu, Co, Ni, or Cr pollution in the River or Delta. However, there are strong indications of anthropogenic inputs of particulate phase Pb, Cd, and Zn. The sedimentary record shows a 60 per cent increase in Pb and a 100 to 200 per cent increase in Cd over the past century; and present-day river particulates are greatly enriched in Pb, Cd, and Zn. Most of the particulate matter settles out very quickly upon entering the ocean; thus only a small percentage (<1%) of the Gulf of Mexico has Pb- and Cd-contamination sediments.

REFERENCES

1. Brewer, P. G. 1975. Minor Elements in Sea Water. In: Chemical Oceanography, Vol. 1, (eds. J. P. Riley and G. Skirrow), Academic pp. 415-496.

2. Brooks, J. M. 1976. The Flux of Light Hydrocarbons into the Gulf of Mexico via Runoff. In: Marine Pollutant Transfer, (eds. H. L. Windom and R. A. Duce), D. C. Heath and Company, Lexington, Massachusetts. pp. 185-200.

3. Curtis, W. F., J. K. Culbertson, and E. B. Chase. 1973. Fluvial Sediment Discharge to the Ocean from the Conterminous United States. U. S. Geol. Surv. Circ. 670, 17 pp.

4. Dyrssen, D., C. Patterson, J. Ui, and G. F. Weichart. 1972. Inorganic Chemicals. In: A Guide to Marine Pollution, (ed. E. D. Goldberg), Gordon and Breach Sci. Pub. pp. 41-58.

5. Edgington, D. N., and J. A. Robbins. 1976. Records of Lead Deposition in Lake Michigan Sediments Since 1800. Environ. Sci. Technol. 10, 266-273.

6. El-Sayed, S. Z. 1975. Texas A&M University, personal communication.

7. EPA Ocean-dumping Criteria. 1973. Federal Register 38, 12872-12877.

8. Everett, D. E. 1971. Hydrologic and Quality Characteristics of the Lower Mississippi River. Louisiana Dept. Public Works U. S. Geol. Survey. 48 pp.

9. Garrels, R. M., and F. T. Mackenzie. 1971. Evolution of Sedimentary Rocks, W. W. Norton. 397 pp.

10. Giam, C. S., H. S. Chan, and G. S. Neff. 1976. Concentrations and Fluxes of Phthalates, DDTs, and PCBs to the Gulf of Mexico. In: Marine Pollutant Transfer, (eds. H. L. Windom and R. A. Duce), D. C. Heath and Company, Lexington, Massachusetts. pp. 375-386.

11. Goldberg, E. D. 1957. Biogeochemistry of Trace Metals. In: Treatise on Marine Ecology and Paleoecology, Vol. I, (ed. J. W. Hedgpeth), Geol. Soc. Am. Mem. 67, Washington, D. C. pp. 345-358.

12. Goldberg, E. D. 1965. Minor Elements in Sea Water. In: Chemical Oceanography, Vol. 1, (eds. J. P. Riley and G. Skirrow), Academic. pp. 163-196.

13. Horowitz, A., and B. J. Presley. 1976. Trace Metal Concentrations and Partitioning in Zooplankton, Neuston, and Benthos from the South Texas Outer Continental Shelf. Arch. Environ. Pollut. Tixcol. (in press).

14. I.D.O.E. 1972. Baseline Studies of Pollutants in the Marine Environment. Natl. Sci. Found., Washington, D. C. 799 pp.

15. Iseri, K. T., and W. B. Langbein. 1974. Large Rivers of the United States. U. S. Geol. Surv. Circ. 686, 10 pp.

16. Leifeste, D. K. 1974. Dissolved-solids Discharge to the Oceans from the Conterminous United States. U. S. Geol. Surv. Circ. 685, 8 pp.

17. Martin, J. H., and G. A. Knauer. 1973. The Elemental Composition of Plankton. Geochim. Cosmochim. Acta 37, 1639-1653.

18. Menzel, D. W. 1974. Primary Productivity, Dissolved and Particulate Organic Matter, and the Sites of Oxidation of Organic Matter. In: The Sea, Vol. 5, (ed. E. D. Goldberg), Wiley-Interscience. pp. 659-678.

19. National Academy of Science. 1975. Assessing Potential Ocean Pollutants. NAS, Washington, D. C. 438 pp.

20. Shokes, R. F. 1976. Rate-dependent Distributions of Lead-210 and Interstitial Sulfate in Sediments of the Mississippi River Delta. Tec. Rep. 76-1-T, Department of Oceanography, Texas A&M University, 122 p.

21. Sims, R. R., Jr. 1975. Selected Chemistry of Primary Producers, Primary Consumers and Suspended Matter from Corpus Christi Bay and the Northwest Gulf of Mexico. M. S. Thesis, Texas A&M University, College Station, 65 pp.

22. Taylor, S. R. 1964. Abundance of Chemical Elements in the Continental Crust: A New Table. Geochim. Cosmochim. Acta 28, 1273-1285.

23. Trefry, J. H., and B. J. Presley. Heavy Metals in Sediments from San Antonio Bay and the Northwest Gulf of Mexico. Environ. Geol., Vol. 1, pp. 283-294.

24. Turekian, K. K. 1969. The Oceans, Streams and Atmosphere. In: Handbook of Geochemistry Vol. I, (ed. K. H. Wedepoh), Springer-Verlag, Berlin. pp. 297-323.

25. U.S. Army Corps of Engineers. 1950-1975. Stages and Discharges of the Mississippi River and Tributaries and Other Watersheds in the New Orleans District. U. S. Army Corps of Engineers, New Orleans.

26. Vinogradov, A. P. 1953. The Elementary Chemical Composition of Marine Organisms. Sears Found. for Mar. Res., Yale Univ., New Haven, Connecticut. 647 pp.

OIL PRODUCTS IN SURFACE LAYERS OF THE PACIFIC AND INDIAN OCEANS

M. Nesterova, I. Nemirovskaya, N. Anufrieva,
and V. Maslov
Oceanological Institute of the U.S.S.R. Academy of Sciences

Among the many aspects of ecological problems of environmental protection, one of the most significant is protection of oceans against pollution by oil products. Oil becomes one of the most widespread pollutants of the world's oceans. It is enough to mention that oil products were present in 50 per cent of all samples taken at 1587 stations in different regions of the Pacific and Indian Oceans on research vessels of the Institute of Oceanology of the U.S.S.R. Academy of Sciences. Observations of ocean pollution have been carried out here since 1973. Starting in 1975, research vessels and the analytical laboratory of the Institute began an international project on ocean pollution observations within the framework of OGSOS. The system of oceanic stations in the Pacific and Indian oceans is shown in Fig. 1. It was discovered that even in the places where there is no oil film on the surface of the water or on the surface of buoys, the S-W part of the Pacific Ocean was covered by small oil-tar balls. In the Indian Ocean, oil products in surface layers were discovered on two of four polygons, and oil-tar balls were present in three others. Data, obtained from the sensor for remote sensing of oil film on the ocean surface (a device developed in the Institute of Oceanology), are very representative: 315 of 3500 miles of the vessel's run in the NW part of the Pacific Ocean were covered with oil film. This finding confirms that the hazard of toxic pollution of ocean waters is real.

Pollution of the seas and oceans by oil products results mainly from discharge by tankers in the ocean of oil-containing (ballast and cleaning) water. Fields of pollutants are observed along the main routes of oil transportation in the seas and oceans. We have no reason to suppose that drainage of oil-containing water from tankers will decrease in the future because the volume of oil transportation increases every year: in 19734 it was 84 million tons; 1949, 151 million tons; 1958, 369 million tons; and, 1968, 1130 million tons. Today the volume of oil transportation is about 2400 million tons. The increase in oil transportation is caused by wide development of oil-based technology. About 40 per cent of the world's energy is obtained from oil and oil products (1).

The losses of oil in the seas and oceans during transportation amount (at present) to 2 million tons per year. Presuming that the present technical level of methods and means of prevention of sea pollution by oil remains at the same level, the discharge of oil from tankers into seawaters will reach the figure of 6 million tons per year by the end of this century.

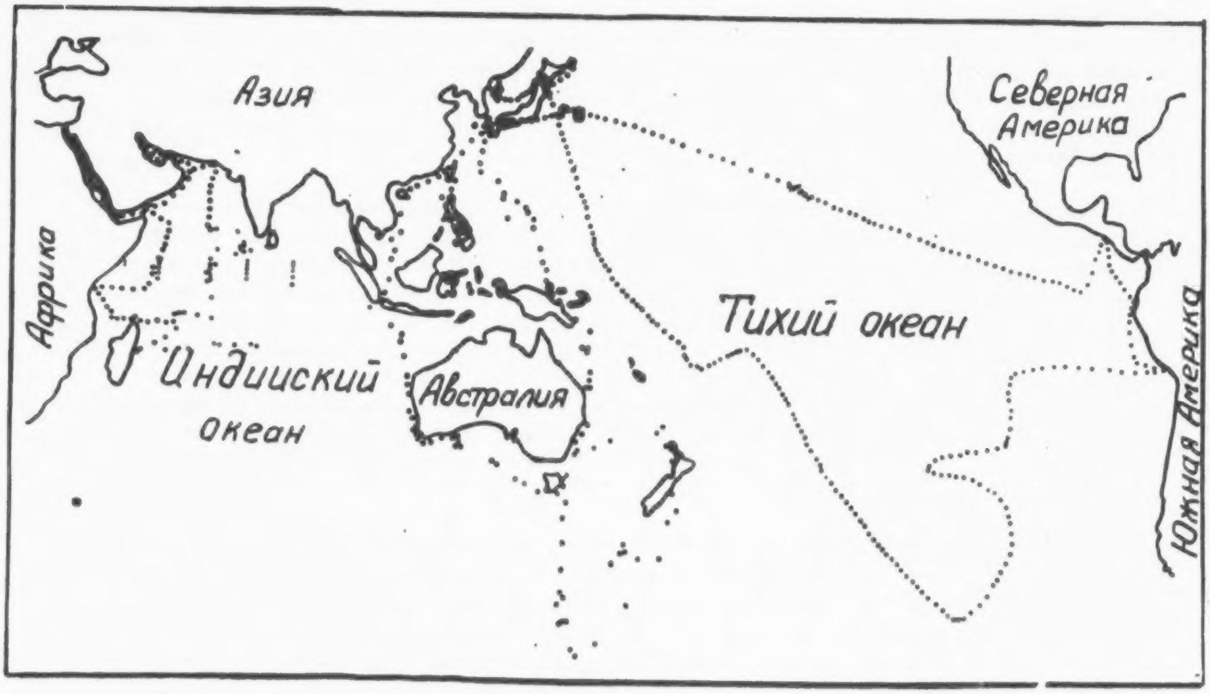


Figure 1. The system of oceanic tracking stations is shown in the Indian Ocean (left) and in the Pacific Ocean (right).

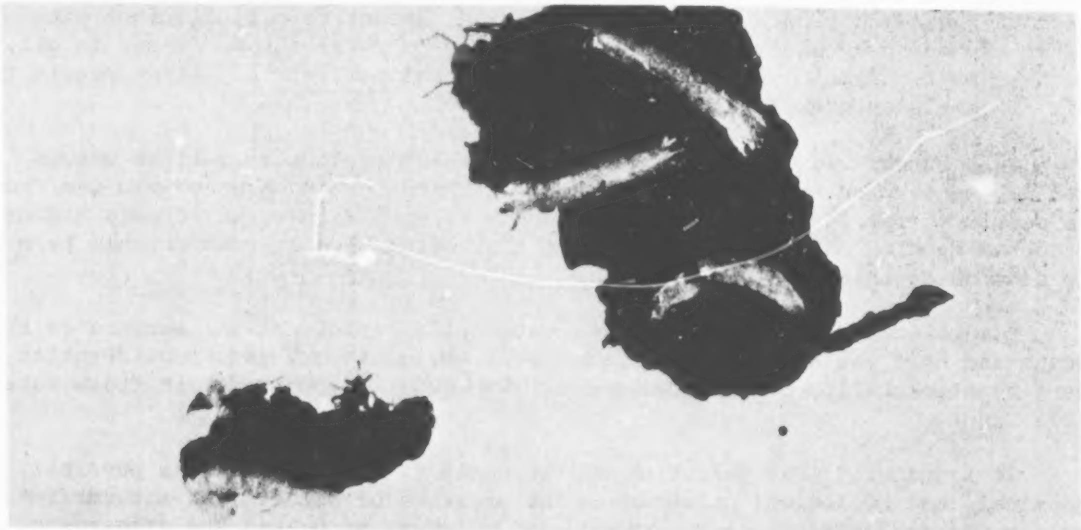


Figure 2. Structured formations, sometimes used by hydrobionts as carriers, were found in surface waters.

Oil pollution of the world's oceans is also up because of the increase in oil production on the continental shelf. In 1970 the volume of oil produced on the shelf was 440 million tons, i.e. one-sixth of the total volume of oil produced. In 1980 it will be 1300 million tons, i.e. one-third of the total volume of oil production planned. Oil leaks happen during oil production in underwater oil fields. It is enough to recall the oil leak in Southern California (Santa Barbara region), which resulted in the mass death of fish and marine organisms.

Damage in oil fields and on tankers are most hazardous as they have extreme influence on ecological systems of separate regions of the world's oceans. We shall mention one more "catastrophy" of the century, the catastrophy of the Torrey Canyon, which has shown the danger impending for whole regions of the planet and the lack of means to avoid such a hazard. Potentially, such hazards always exist due to the increase of tonnage and speed of tankers. Nineteen tankers sank in 1976, with two times more tonnage than those which sank in 1975. Five tankers sank in two weeks (15 to 31 December) near the coast of the U.S. During eight months of 1976, the amount of oil discharged was 198277 tons. About 20 to 30 per cent of the total pollution in the seas is caused by oil.

Oil-containing industrial and municipal waste waters, carried to the seas by rivers, are also an antropogenic source of pollution. The total amount of oil and oil-product pollution of the world's oceans, according to various authors, is estimated to be from six to ten million tons per year. It is obvious that the ocean cannot cope with such intensive pollution. The presence of oil products in ocean waters confirms the theory that processes of ocean pollution prevail over processes of the pollutant's chemical and biological decomposition.

Oil spilled in the sea produces a film on the surface due to the influence of waves and wind. When there is a great amount of oil, it mixes with water producing an emulsion. These are mainly of reverse type "water in oil," such as high-molecular substances (resins, asphaltens, etc.). Also present in oil are emulsion stabilizers of various types.

Such structured formations may exist for a long time in surface waters and may be carried by currents over long distances. Some hydrobionts use them as carriers (see Fig. 2). When the density of such formations becomes higher than the density of water, they sink to the bottom, causing considerable harm to benthos organisms.

Low-molecular oil compounds evaporate quite rapidly on the surface of the ocean and have low solubility in seawater. One must take into consideration here that solubility of hydrocarbons in seawater is lower than in fresh water (2).

It is natural that pollution of the world's oceans influences physical, chemical, and biological processes. The presence of oil film on the surface breaks the exchange of energy, gases, and moisture of oceans and atmosphere. One must also remember that one-half of the oxygen of our planet is produced by the ocean. Heat energy of the ocean is one of the important factors of climate formation. The presence of oil film on the surface of the ocean might influence weather conditions, but this has not been studied yet and needs further detailed investigation. By experiments, we determined that one square mile of ocean evaporates 97 tons of water per hour. When oil film is present, the amount is only 48 tons per hour.

It is not necessary to mention the fact of the fatal influence of oil on hydrobionts.

All the above mentioned facts were determined by investigations of pollution of the world's oceans in the Institute of Oceanology. They included development of methods and means of protection of the sea from pollution by oil and measurement of pollution levels (3,4).

At present it is impossible to determine accurately and quantitatively the oil pollution of seas and oceans. This is caused not only by analytical difficulties in determining oil products in seawater, but also by not having sufficient comprehension of all processes which influence oil products in the seas and oceans. Analytical difficulties are caused by the fact that oil products are a very complex mixture of different compounds. The quantitative content in oil depends on the oil field. Oil product output also depends on the process of refining. At the same time, these compounds are very close to some natural compounds present in seawater as a result of the activity of marine organisms. Absence of a unified methodology of determination of oil hydrocarbons does not permit the possibility of comparing the results of different investigations and drawing conclusions on changes in pollution of certain regions of the world's oceans. This is especially the case when it is necessary to determine the results of measurements of prevention of sea and ocean pollution by oil and oil products.

When conducting an international experimental project of studying oil pollution of the marine environment, two methods, fluorescent and IR-spectrohotometry, are used. The fluorescent method is the most sensitive. But when using this method for determination of oil products in seawater, one should take into consideration that fluorescence of oil depends on many aspects (composition, transformation of substance under the influence of environment, wave length λ exitation, λ registration, and so on), which makes it very difficult to compare the results obtained. In our tests we studied spectra of exitation and spectra of fluorescence of oil products and crude oils from different oil fields of the USSR, Iran, and Vietnam. The first data obtained give us a method to assess the presence of hydrocarbons in the waters of the Pacific and Indian Oceans.

Measurements of hydrocarbons in ocean waters were performed by IR-spectrophotometry.

The study was conducted during the 12th and 13th cruises of the Dmitri Mendellev, and the 56th cruise of the Vitiaz in the Pacific Ocean, Sea of Japan, and Okhotsk Sea. Three hundred and twenty samples were taken during six tests in the Pacific Ocean and Sea of Japan. In the open areas of the Pacific Ocean and Sea of Japan, hydrocarbons were not detected. This can be explained by the fact that in the warm part of the year, when studies were conducted, decomposition of non-polar hydrocarbons is most intensive (5). There were some exclusions, for example when content of hydrocarbons in the samples amounted to 60-80 mg/ℓ. These local contaminations are possibly the result of the discharge of cleaning water from tankers. Hydrocarbons were found in the island (up to 3900 g/ℓ), and in the zone of intense navigation, Sangar Strait (130 to 150 g/ℓ). Only two of 40 samples taken in Okhotsk Sea showed the presence of hydrocarbons (50 g/ℓ).

Studies in the Pacific Ocean were continued in the 14th to 16th cruises of *Dm. Mendellev* (Feb. to May and July to Sept. 1975, Dec. 1975 to March 1976) and in the 59th cruise of the *Vitiaz* from May to June 1976.

Hydrocarbons were found in surface waters of the SE part of the Pacific Ocean, mainly in equatorial zone (30°NL to 20°SL), where their concentration differed from 50 to 1460 g/ℓ. Hydrocarbon content in all samples from the Western tropical zone of the Pacific Ocean were from 90 to 380 g/ℓ. On the polygon, in the NW part of the Pacific Ocean (39°NL to 34.5°NL; 146.9° to 150°EL), hydrocarbons were only found in 24 samples (in concentrations of 80 to 340 g/ℓ).

In the Sea of Japan and the NW part of the Pacific Ocean, the concentration of hydrocarbons changed from 0 to 380 g/ℓ. In the 63 of 123 samples, hydrocarbons were not present. In the southern part of the Sea of Japan in the region of Honshu Island and in Sangar Strait, hydrocarbons are present in concentrations of 240 to 280 g/ℓ.

The biggest concentration of hydrocarbons in the SE part of the Pacific Ocean was detected in port areas of Singapore, 7060 g/ℓ, Freemantle, 1040 g/ℓ, and in the seaways near western Australia in the region of Iawa Island, 1000 g/ℓ. In the Fiji and Tasman Seas, hydrocarbons were seldom found.

Practically no data are available concerning distribution of tar balls in the Pacific Ocean. Investigators (5) have shown that the range of concentrations of tar balls in the NW part of the Pacific Ocean lies in the limits of 0.3-14 mg/m^2 to 0-2.9 mg/m^2, in the NE part. Maximum concentrations are found in Kurosivo Stream.

It is natural that we cannot draw the conclusion based on the small number of measurements taken, that the western part of the Pacific Ocean is more polluted than the eastern part, as the distribution of tar balls is not stable and is non-uniform.

In January to March 1974, studies of the equatorial part of Indian Ocean were conducted on board r/v *Vitiaz*. Samples were taken on four polygons 85°EL, 75°EL, 65°EL, 54°EL, sections from 4°SL to 4°NL. Hydrocarbons were found on the first and the second polygon, i.e. in the eastern part of the region. The maximum concentration of 1130 g/ℓ was found on the first polygon. We found a general tendency of some non-uniform decrease in the concentration of hydrocarbons with depth, excluding two stations on the second polygon (0°55'S, 74°49'E), where the concentration in the surface layer was equal to 160 g/ℓ. At 100 m it increased to 240 g/ℓ and at 200 m was 850 g/ℓ. In the western part of the equatorial zone of the Indian Ocean, hydrocarbons were not found in surface waters, but tar balls were present. Relatively high hydrocarbon contents in the eastern part of this region, which lays far from ship lanes, may be explained by hydrodynamic conditions of this part of the ocean (the zone of surface streams). In winter, this region is the area of the southern periphery of the western monsoon stream, and the northern part of the equatorial counter stream. The velocity of monsoon stream increases from the east to the west (from 40 to 120 cm/sec). The hydrocarbons are probably transported from the dynamically active western zone and are accumulated in the relatively calm eastern zone.

The NW part of the Indian Ocean was studied in March to June of 1976 by r/v Academician Kurchatov in five sections: along the African coastline, a quasizonal section along 8°SL, a meridianal section along 65° to 67°EL, and two small sections on the Oman and Aden Gulfs.

The concentration of hydrocarbons in the surface layers of Bab-al-Mandeb Strait, and along the African coast, changed from 0 to 350 g/ℓ. In 42 per cent of the samples, hydrocarbons were not detected. On the longitudinal section, hydrocarbons were absent in 2 of the 16 samples. The concentration in samples taken near Madagascar reaches the value of 80 to 320 g/ℓ. Determination of oil-oxidizing bacteria corresponds with the data on hydrocarbon concentration. On the section Sokotra to Mombasa, bacteria were not present in the surface layer. The maximum bacteria concentration was found in the region of the Port of Mombasa (200 to 300 g/ℓ). On the latitudinal section, oil-oxidizing bacteria was found near the northern part of Madagascar.

On the meridional section we found a non-uniform increase in the concentration of hydrocarbons in a northerly direction. In the southern part of the section (in the region of the South Subtropic convergence), hydrocarbons were not found. From 15°SL, we found an increase of hydrocarbon concentrations from 14° to 2°SL. In the region of the equator, the concentration is equal to 130 g/ℓ.

From 11° to 18°NL hydrocarbons were not found, but then they appeared in concentrations of up to 2870 g/ℓ. This change of concentration corresponds to the dynamics of the region. The southern part of the Arabian Sea is very active dynamically.

In the Oman and Persian Gulfs, the concentration of hydrocarbons reached 1000 g/ℓ. The maximum concentration was found in the region of El-Kuwait, and in the Oman Gulf. The quantity of hydrocarbons decreases slightly with depth. In the Persian Gulf, a large concentration of hydrocarbons corresponded to the maximum quantity of oil-oxidizing bacteria. In Aden Bay, the quantity of hydrocarbons was also rather large. The maximum content of hydrocarbons was found near the coast of the Arabian Peninsula, and in the central area the content decreased to 420 g/ℓ. Approaching the African coast, we found some increase but did not notice a decrease of the concentration with depth. We think that the waters near the Arabian Peninsula are of Persian-Arabian origin, which explains the presence of hydrocarbons. In March 1976, hydrocarbons were found in 11 of 17 samples in concentrations not more than 300 g/ℓ. In June 1976, hydrocarbons were found in 13 of 16 samples in concentrations from 0 to 2260 g/ℓ. In March, 1976, oil spots in the Red Sea were seen only once (in June). An oil-film of yellow-green, brown, and grey color covered a considerable part of the surface of the sea.

Thus, the studies of surface waters for hydrocarbons show the presence of hydrocarbons in the Pacific and Indian Oceans. The concentration of hydrocarbons depends on the anthropogenic, hydrodynamic, hydrobiological, and other factors. The studies should be continued. The prognosis of seawater quality may be done only on the basis of systematic, complex studies of seawater pollution. Under these conditions, recommendations on the protection of the world's oceans can be prepared.

REFERENCES

1. Nunuporv, S.M. 1971. Prevention of Marine Oil Pollution. Transport, Moscow.

2. Goldberg, E.D. 1975. Health of the Oceans. USA.

3. Nesterova, M.P. 1972. Prevention of Marine Oil Pollution When Cleaning Tankers.

4. Nesterova, M.P. 1976. Surface Radioactive Substances and Their Role in Solving Several Marine Ecology Problems. Proceedings of the International Symposium on Substances Contained in Water-Toxic Substances in the Baltic Sea. Rostok GDR.

5. Nelson-Smit. 1973. Marine Oil Pollution. GIDROMETIZDAT, Leningrad.

OIL POLLUTION STUDIES IN THE NORWEGIAN AND GREENLAND SEAS

V. M. Smagin and V. S. Rachkov
The Arctic and Antarctic Research Institute, Leningrad

Oil pollution of the world's oceans has become the subject of special concern to various national and international research organizations within the International Pilot Project on Marine Pollution Monitoring. This project envisages study of water surface contamination by petroleum products of the North Atlantic, the Norwegian and Barents Seas, thus providing us with a possibility to study processes of pollutant transport, including a current system from the Atlantic to the Arctic Ocean. The need for such a study seems to be quite obvious. Once oil has entered the high latitude seas it would accumulate there due to slow degradation processes at low temperatures. An oil spill on the Arctic ice could significantly change the radiational balance of the underlying surface as a result of sharp decrease in ice albedo which in turn could cause considerable climatic effects on the whole region.

Before handling the problem of oil pollution in the observed region, it is necessary to outline briefly some features of its hydrometeorological regime.

The hydrometeorological regime of the Norwegian and the Greeland Seas is rather complex. It has large seasonal variations and it is affected by the following main factors:

1) influence of the warm Atlantic waters from the south.
2) influence of the cold Arctic waters from the north.
3) presence of the Norwegian and Greenland water gyrals inducing the upwelling of the bottom water masses.
4) presence of stable and seasonal (winter) hydrofronts.
5) effects of the Icelandic Low and the Arctic High.

A complex hydrological regime, and its seasonal variability, determine the character of the hydrochemical water regime of the region. Oceanic and atmospheric processes appear to also affect the conditions of pollution fields, their spatial and time variations.

During the period of 1975 to 1977, the Arctic and Antarctic Research Institute (AARI) carried out a series of oil pollution studies of the surface waters in the North Atlantic, the Norwegian and Greenland Seas. The analysis of oil samples was performed by the infra-red spectrophotometry method with only dissolved and emulsified hydrocarbons being defined. Sample filtration, however, to avoid microscopic tar balls, was not made. Sample of 2ℓ marine water samples was made at 1 m depth in accordance with the recommendations of the IOC/WMO Pilot Project on Marine Pollution Monitoring. During sampling, care was taken to avoid contamination of seawater samples by petroleum films.

The hydrocarbon extraction was made at the ship laboratory by CCl_4. The extracts were placed into glass flasks with tight stoppers under a 1-cm water layer. The solvent and the flasks were prepared at the laboratory and thoroughly tested. The final analysis by infra-red spectrophotometer was also performed at the AARI laboratory.

Sampling for tar balls was made by Neuston net towed by a ship according to IOC/WMO Pilot Project recommendations.

The data obtained on petroleum hydrocarbons, or to be more exact, on non-polar hydrocarbons, in the surface waters of the North Atlantic, the Norwegian and Greenland Seas during the 1975-1977 period, refer to different seasons. Unfortunately it was not possible to carry out studies during all seasons of the year which implies certain difficulties with data comparison.

Most of the data was obtained in the spring. Figure 1 shows hydrocarbon content observed in the North Atlantic in the spring 1975. In some cases an increase of the maximum permissible concentration of hydrocarbons was observed, with concentration in the Atlantic waters then moving to the Norwegian Sea. The amount was less than 30 μg/ℓ, (i.e.,below the limit for the sensitivity of the determination method).

In the spring of 1976, studies of surface water petroleum pollution of the Norwegian and Greenland seas were made simultaneously from aboard two AARI research vessels. The observations covered the whole water area of the Norwegian Sea and the ice-free area of the Greenland Sea (Fig. 2, 3). It is worth mentioning here that despite the increased hydrocarbon content (more than 30 μg/ℓ) in some areas, no extensive pollution fields were found in the region. Even in areas with an increase in hydrocarbon content there was large non-uniformity in the distribution. In a number of adjacent sampling areas the hydrocarbon content was either higher or lower than 30μg/ℓ. According to data obtained in March of 1976 by the r/v Professor Zubov (Fig. 2), the largest density of values exceeding 30 μg/ℓ was observed in the Greenland Sea in waters adjacent to the northern coast at a section along the 70° latitude (i.e.,at the boundary of the Norwegian and Greenland water gyrals). In May, at the eastern periphery of the Greenland circulation, a patch of oil with a hydrocarbon level exceeding 60 μg/ℓ was detected.

Unlike the data obtained by the r/v Professor Zubov, which operated mainly in the Greenland gyral area, the data obtained in spring of 1976 by the r/v Professor Viese covered almost the whole water area of the Norwegian Sea. The observations were sufficiently frequent to allow us to assess the level of surface water oil pollution (Fig. 3). It turned out that the central part of the Norwegian Sea was less contaminated (the regions of the Norwegian circulation),but at its northern and southern peripheries the hydrocarbon concentrations were found to exceed 30 μg/ℓ. In the southern part of the sea the hydrocarbon concentrations were lower than 30μg/ℓ. However, on several occasions in the Norwegian current, their increase was observed. Particular attention should be given to the region near the Norwegian coast between 67° and 70°S, where the hydrocarbon content exceeded

30μg/ℓ. In the Nordkapp current waters the hydrocarbon content did not exceed this value.

In the summer of 1976, data from the r/v Professor Viese disclosed the largest hydrocarbon concentration in surface waters of the Norwegian Sea. The oil was observed in the southern part in areas adjacent to the North Sea, Faeröe-Shetland Channel and Faeröe-Iceland Strait (Fig. 4). In the area of 68° to 70°S, near the Norwegian coast, the hydrocarbon concentration remained large.

In the winter period of 1977 the observations of hydrocarbon content were carried out on board of the r/v Professor Viese (Fig. 5). The data obtained on this cruise show that in winter, the hydrocarbon concentration did not exceed 30 μg/ℓ, with the exception of two stations: one in the Shetland Islands area (hydrocarbon content - 40 μg/ℓ, the other in the Faeroes Islands area (hydrocarbon content - 130 μg/ℓ).

During this voyage in the Greenland and Norwegian seas and also in the Faeröe-Iceland Strait, surface layer trawling by a Neuston net was performed to detect tar balls. The analysis indicated that in all samples taken, there were no tar balls present.

The comparison of 1976-1977 data has shown that in the winter of 1977 the hydrocarbon content in surface waters of the North-European basin was lower than that in the summer of 1976. The hydrocarbon content in most samples was within the limit of the sensitivity of the analysis method. This decrease cannot be attributed to seasonal variations, nor can we suggest a pollution decrease trend. It should be noted here that most samples with higher hydrocarbon content were taken in light winds and small swells except in coastal areas and at sampling sites in the island area. During winter studies of 1977 optimum conditions for surface water mixing down to a deeper depth were observed. Wind speed in general exceeded 10 m/sec., and the wave height was about 1.5 m. Therefore, organic substance present in marine water, observed in light wind and on the sea surface as film, can interfere with hydrocarbon determination. Therefore, to determine petroleum hydrocarbon content in the waters of the Norwegian and Greenland seas it is desirable to use methods more sensitive and selective than infra-red spectrophotometry. That is why such methods are luminescence spectrometry and gas chromotography are used, at present. The following conclusions can be drawn from the above:

1) Studies performed by the AARI in 1975-1977 showed the hydrocarbon content in the surface layer almost over the entire Norwegian and Greenland seas to be less than 30 μg/ℓ.

2) The highest hydrocarbon content was in the surface waters of the Norwegian circulation in the southern area of the sea and off the Norwegian coast in the area between 68° and 70°N.

3) The highest hydrocarbon content in the surface waters of the Greenland sea was found in peripheral areas of the Greenland circulation and waters adjacent to the northern coast of Iceland.

4) The hydrocarbon level in the North Atlantic current surface waters is too low to form pollution fields in the region, but the effect of the North Sea waters in this respect might be decisive.

5) Waters of the Spitsbergen and the Nordkapp current have lower hydrocarbon concentrations and cannot be considered as a source of oil pollution of the Arctic basin waters.

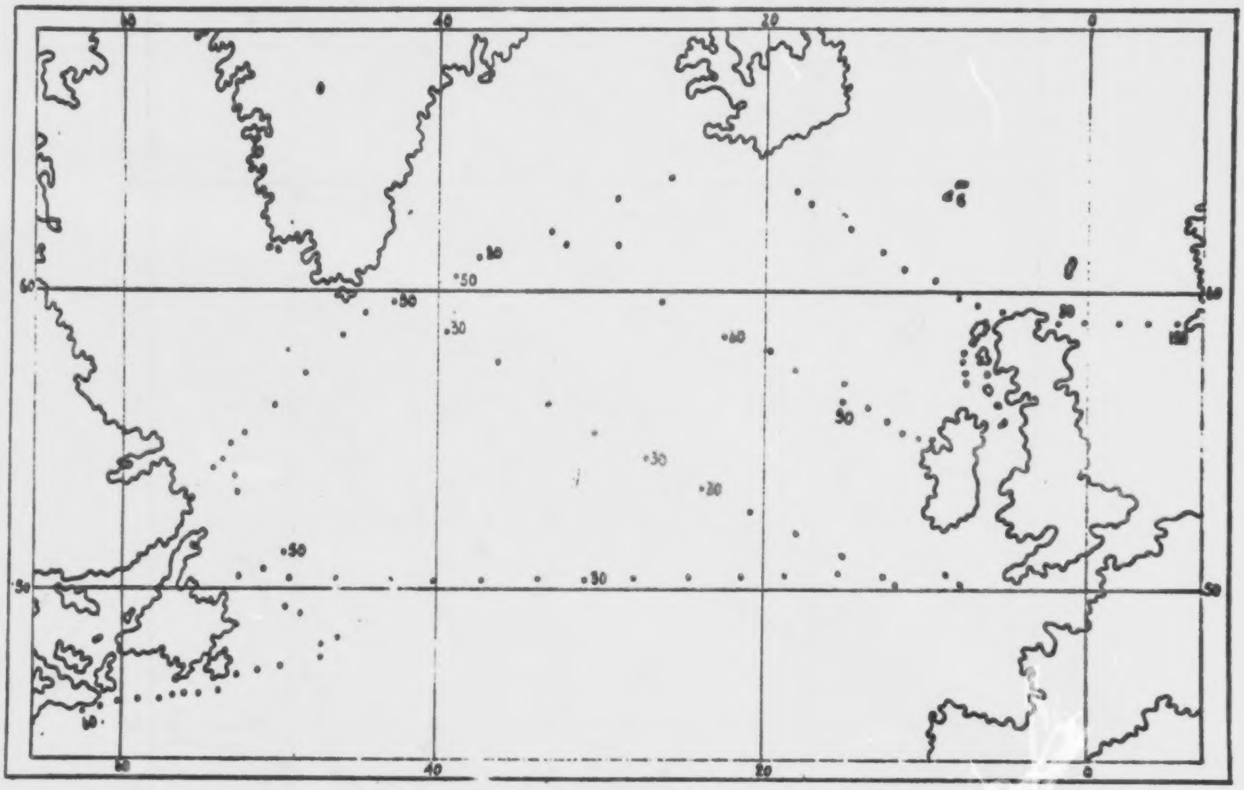


Figure 1. North Atlantic hydrocarbon content (μg/ℓ) during 4 April to June 6, 1975.

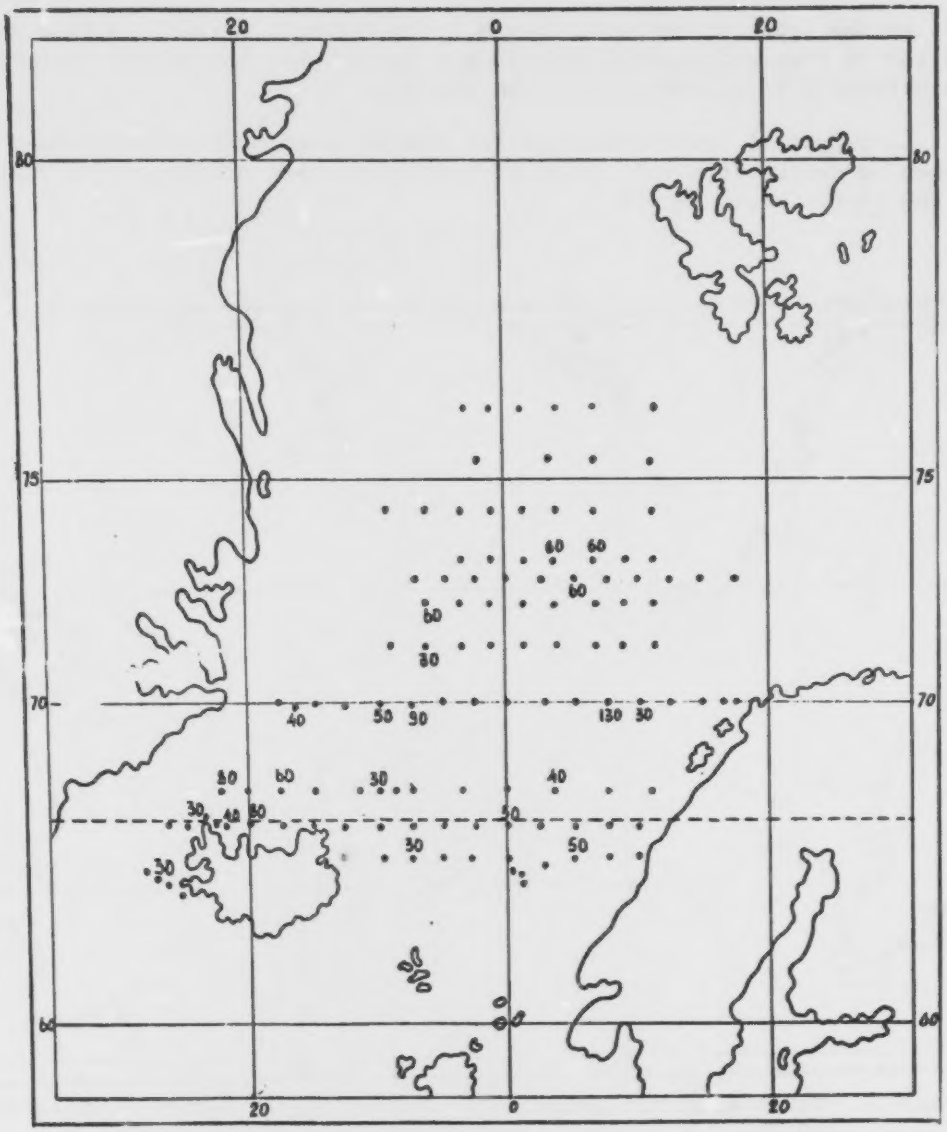


Figure 2. The hydrocarbon distribution (μg/ℓ) at 1 meter depth from 13 March to 28 May 1976, on the 19th cruise of the R/V Professor Zubov.

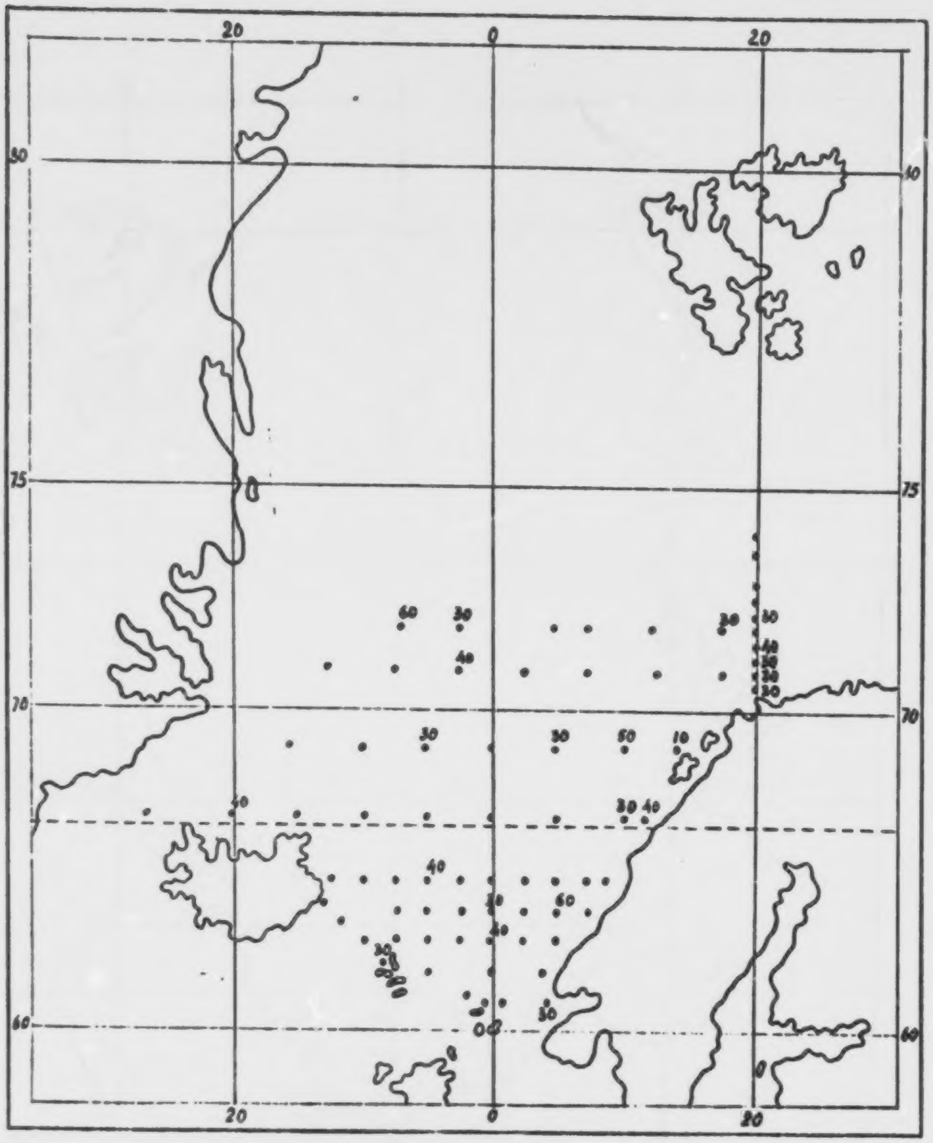


Figure 3. The hydrocarbon distribution (μg/ℓ) at 1 meter depth in spring 1976, on the 25th cruise of the R/V *Professor Viese*.

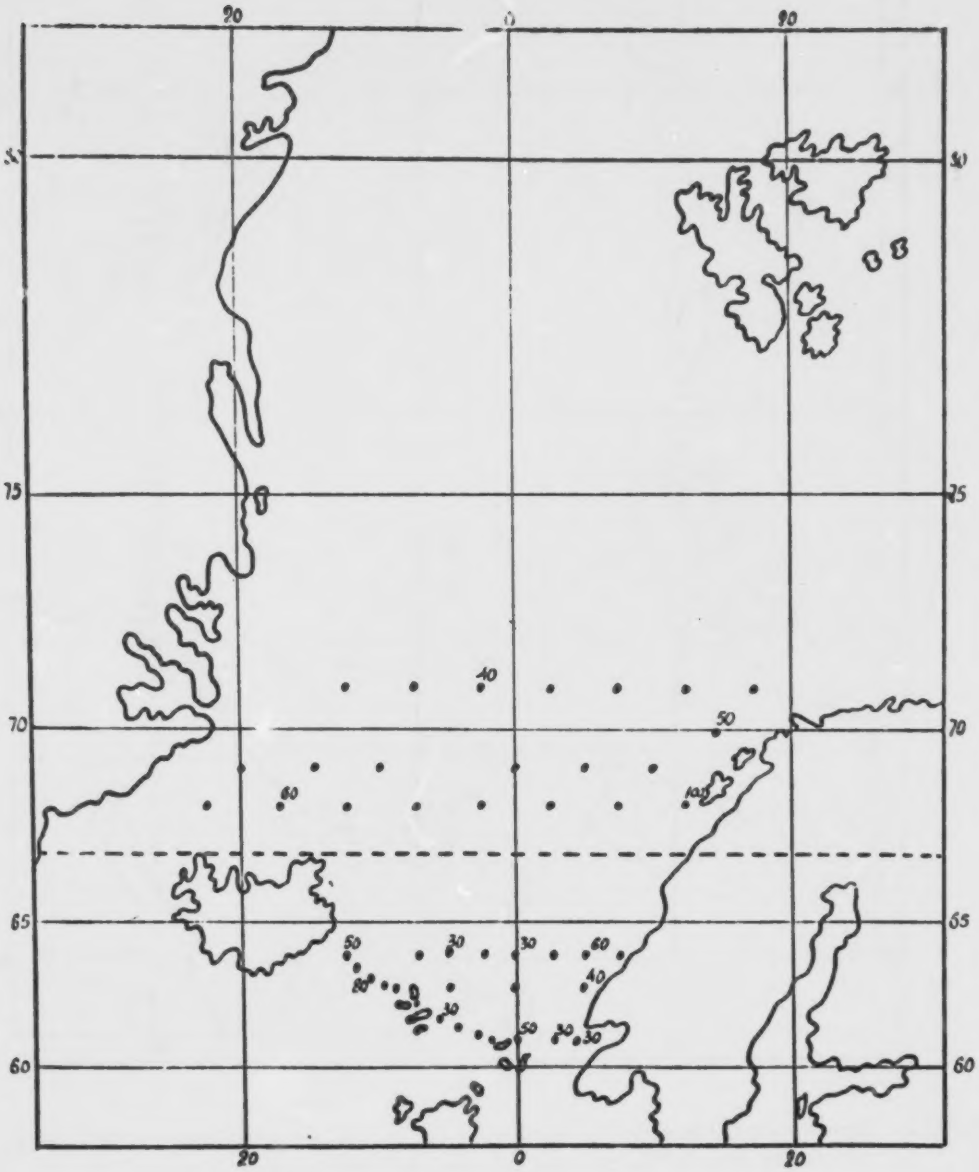


Figure 4. The hydrocarbon distribution (μg/ℓ) at 1 meter depth in summer 1976, (17 June to 13 July 1976) on the 25th cruise of the R/V Professor Viese.

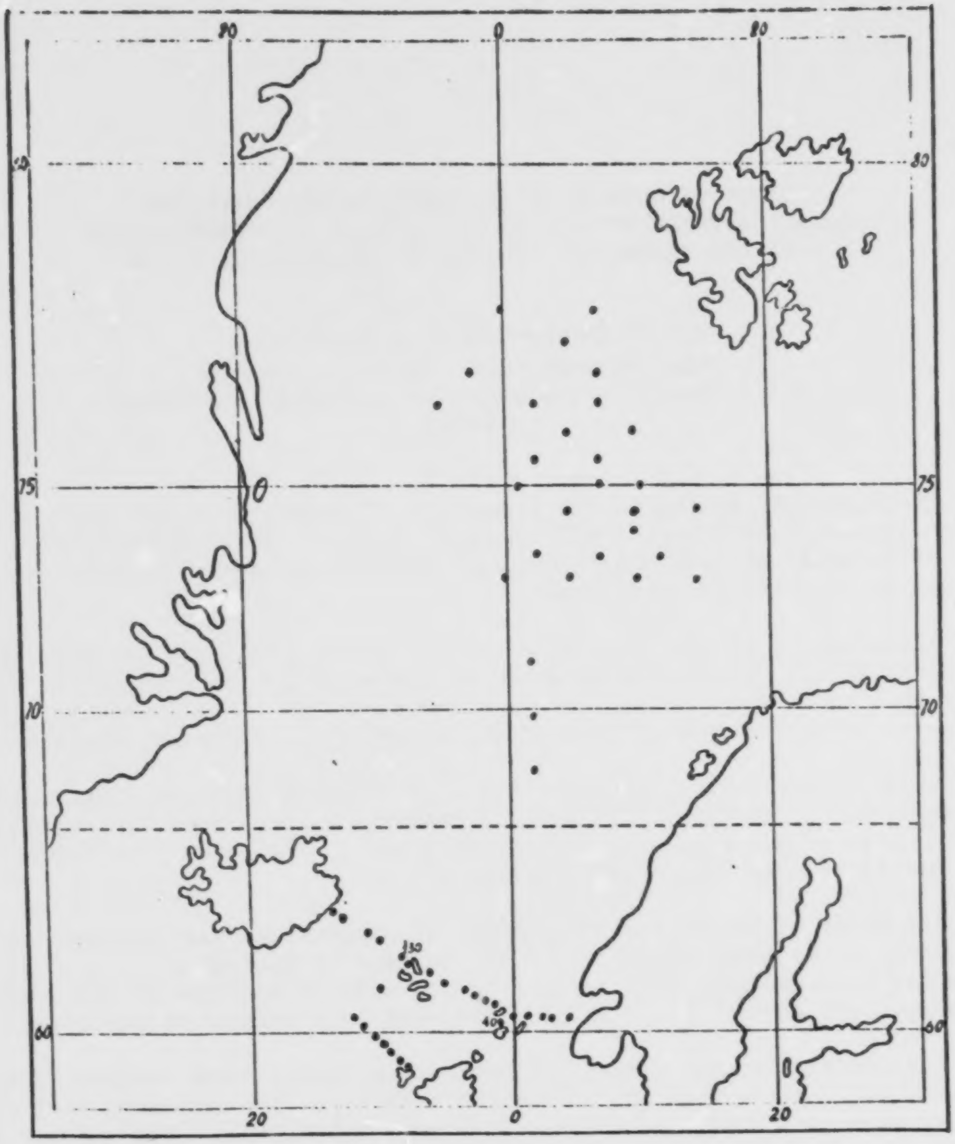


Figure 5. The hydrocarbon distribution (μg/ℓ) at 1 meter depth in winter, 1977, (27 December 1976 to 1 March 1977) on the 27th cruise of the R/V Professor Viese.

STUDY OF METHODS OF SAMPLING SEAWATER FROM THE OCEAN'S SURFACE MICROLAYER AND RESULTS OF DETERMINATION OF OIL IN VARIOUS REGIONS OF THE ATLANTIC OCEAN

V.I. Mikhaylov and S.G. Oradovskiy
State Oceanographic Institute, Moscow
Odessa Branch of the State Oceanographic Institute
Odessa

Questions pertaining to the properties of seawater at the ocean-atmosphere interface have been insufficiently studied. This is due to the fact that it is still unclear what should be regarded as the surface microlayer and how to estimate its thickness.

According to recent investigations (6,10,12,13,15), the distinctive character of the chemical composition of the water of the ocean's surface layer applies only to a thin layer comparable to the electric double layer, i.e., its thickness does not exceed the diameter of ten water molecules.

Data of experimental studies (4,9,11,14), shows that the distinctive character of the surface microlayer of seawater extends over thousands of angstroms or more. Depending on the character of the waves, the thickness of this microlayer can vary from 5.10^{-3} to 0.1 cm.

The study of the surface microlayer is hampered in many respects by the difficulties involved in taking the samples of surface seawater. According to literature data, only a few methods of sampling of the surface microlayer are known (1,2,3,5,7,8), but most have certain disadvantages.

A.V. Tsyban (5) has designed a device for taking water samples from the 0-2 cm layer that is used for collecting bacteria. The receiving part of the device consists of a two-necked 250-cm^3 glass ampoule. The ampoule is lowered in a horizontal position onto the surface of the sea and samples a thin, 2-cm layer of water.

The same principle underlies the operation of a device proposed by G.M. Kogan (3) for sampling seawater from the surface microlayer. The device consists of a flat plexiglas plate measuring 60 x 50 x 10 cm. Foam plastic strips attached to the edges of the plate keep the device in a horizontal position. The lower edge of the device is lowered onto the surface of the water, and while slowly moving forward, it shears off a layer of the surface water no more than 10 cm thick.

A different principle underlies the sampling of seawater by means of a hose sampler (1). The collector of the device consists of a foam plastic floater measuring 20 x 20 x 20 cm with a hole in the middle that accommodates a glass tube. The lower end of the tube is placed at a depth of about 3 cm from the water line of the floater; the upper end is connected by a rubber hose to a jar. A wide-mouth jar closed with a stopper with two bent glass tubes serves as the sampler. The lower end of one of the tubes almost touches the bottom of the jar and is connected by a rubber hose to a Komovskiy vacuum pump. The pump evacuates the jar, and the escaping air is replaced by seawater, which comes in from the collector. By changing the depth of immersion of the glass tube passing through the floater, seawater can be obtained at a distance of 3 cm or more from the sea surface.

The "Afrodita-1" device built by V.I. Timoshchuk successfully embodies the sampling principles developed by G.M. Kogan and V.S. Bol'shakov (4). Purpose of the device is to sample seawater from a drifting or slowly traveling ship in a layer extending from the surface to a depth of a few centimeters. It consists of a collector, pointer, container, vacuum pump, and vacuum and rubber-canvas hoses. The collector consists of two foam plastic floaters which, for greater rigidity and stability, are connected by stainless couplings. Fastened between the floaters is a plexiglas sheet (3 mm thick) with cavities in the shape of funnels ending in couplings. The funnel couplings are connected by vacuum hoses to a T joint that is connected to the container by a rubber-canvas hose. Rudders, which provide for a specified immersion depth of the device and a thickness of the sampled water layer, from 0 to 20 cm, are attached to the lower part of the collector. The thickness of the collected layer of seawater depends on the state of the sea surface, wind velocity, and depth angle of attack.

A simple arrangement for sampling the surface microlayer of seawater by means of a screen was proposed by Garrett (8). The sampler consists of a stainless steel frame over which is stretched a net of the same material. Handles by means of which the sampler is lowered onto the water surface are welded to the frame. The device is lowered onto the water surface from a boat, and after the meshes are filled with water, it is raised. The water occupying the meshes of the screen is poured through a corner of the frame into a receiving container. This device permits the sampling of a surface microlayer of seawater no more than 300 μ thick.

Thus, it may be concluded that each of these sampling methods permits the sampling of different layers of surface water (from 300 μ according to Garrett, and to 10 cm according to Kogan). This makes it impossible to compare the results of analyses of sea and ocean surface waters sampled with different instruments and devices.

In our view the sampler proposed by Garrett is currently the most successful device for sampling water from the layer closest to the ocean-atmosphere interface. However, the material from which the sampler is made does not fully meet the requirements for such devices because it is subject to corrosion, which changes the chemical composition of the seawater sample and distorts the results of findings.

We tested screen samplers made of various materials, i.e., gauze, brass, stainless steel, and nylon. We found that the best results were obtained with nylon. The nylon sampler is based on the principle proposed by Garrett and uses No. 7 nylon screen (with a mesh area of 1 mm^2). The screen is stretched over a frame of noncorroding material. Four guy ropes of fish line attached to the frame are connected to a kapron marline longer than the height of the ship's side.

The sequence of sampling of the surface microlayer by means of this sampler is as follows. To exclude contaminants from the ship, the sampling is carried out immediately after the ship has stopped. The sampler is lowered to the sea surface on the lee side of the forecastle. As soon as the water fills the openings of the screen, the sampler is quickly raised. The sampler raising time is 5 to 6 seconds. On board the ship, the sampler is tilted, and the seawater collected by the meshes is drained into a receiver (jar).

In the winter of 1975-76 we conducted studies in the central and northern Atlantic to estimate the thickness of the sampled microlayer with screen samplers. The work was done under ship laboratory conditions and directly under natural conditions. During the studies, the wind velocity ranged from 2 to 8 m sec^{-1}, and the wave height, from 0.2 to 2.5 m.

Two samplers with an area of 2460 cm^2 and 11079 cm^2 were built. Average results obtained from the determination of the thickness of the sampled surface microlayer of water with screen samplers of different areas are presented in Table 1.

Analysis of the results obtained indicates that independently of the area of the sampler, the thickness of the sampled microlayer is approximately 230 microns. The variation coefficient for samplers with an area of 2460 cm^2 varies from 6.6 to 10%, and for samplers with an area of 11079 cm^2, 4.3%.

It should be noted that the studies were carried out in waters of different salinity (from 29.3% to 37.6%), but this did not affect the thickness of the surface microlayer sampled.

The data of actual measurements of the thickness of the sampled surface microlayer were confirmed by experiments in the ship's laboratory. A model of the screen sampler with an area of 100 cm^2 was prepared for this purpose. The experiments were conducted with seawater of different salinity as well as distilled water. The water temperature varied from 8°C to 26°C. The results of these studies are presented in Table 2.

Analysis of the data of Table 2 suggests that the screen sampler model samples surface microlayers whose thickness is independent of the water

TABLE 1. RESULTS OF DETERMINATION OF THE THICKNESS OF SAMPLED SURFACE MICROLAYER WITH A SCREEN SAMPLER HAVING A MESH AREA OF 1 mm^2

Type of sampler	S	n	v	δ	K	CI	Z	S 0/00
Sampler with nylon screen mesh area 1 mm^2	2460	22	54.3	5.4	10	54.3 ± 4.3	221	37,627
	2460	22	54.4	5.2	9.4	54.4 ± 4.7	221	37,520
	2460	23	54.2	4.6	6.6	54.2 4.3	221	33,827
	11079	21	247.0	10.8	4.4	247.0 13.1	222	37,580
	11079	24	247.0	10.2	4.2	247.0 12.2	222	33,827
	11079	22	247.0	10.1	4.2	247.0 12.2	222	29,342

Symbols:

n - number of determinations

v - average amount of water collected at one time, cm^3

δ - rms deviation, cm^3

S - area of sampler, cm^2

K - variation coefficient, %

CI - confidence interval, cm^3

Z - thickness of sampled layer, microns

S $^0/00$ - salinity of sample, $^0/00$

TABLE 2. RESULTS OF DETERMINATION OF THE THICKNESS OF SAMPLED SURFACE MICROLAYER OF SEAWATER AND DISTILLED WATER USING A MODEL OF SCREEN SAMPLER UNDER LABORATORY CONDITIONS

Type of sampler	S	n	v	δ	K	CI	Z	$S^0/00$
Model of sampler with a mesh area of 1 mm^2	100	31	2,0	0,03	1,2	2,0 0,04	200	36,980
	100	24	2,0	0,04	1,5	2,0 0,05	200	33,827
	100	21	2,0	0,03	1,4	2,0 0,04	200	36,520
	100	28	2,0	0,03	1,3	2,0 0,06	200	29,342
	100	32	2,0	0,04	1,4	2,0 0,06	200	distillate
	100	37	2,0	0,05	1,5	2,0 0,06	200	distillate

Symbols:

n - number of determination

v - average amount of water collected at one time, cm^3

δ - rms deviation, cm^3

S - area of sampler, cm^2

K - variation coefficient, %

CI - confidence interval, cm^3

Z - thickness of sampled layer, microns

$S\ ^0/00$ - salinity of sample, $^0/00$

salinity and temperature and amounts to 220 microns (variation coefficient, 1.2 to 1.6 per cent.)

To determine the effect of various types of surfactants on the thickness of the surface microlayer sampled, a series of experiments were conducted with surfactant additions to water using a screen sampler with a mesh area of 1 mm^2. Different amounts of the preparation "Novost" and sodium alkylbenzoylsulfate were added to the water samples to concentrations of 1000 $\mu g/\ell^{-1}$ or higher, which were known to be high in comparison with detergent concentrations observed in open water areas of the North Atlantic. The screen sampler model was used to collect samples of these solutions.

Average results of experiments with additions of synthetic surfactants to seawater and distilled water are given in Table 3.

It is evident from Table 3 that the additions of synthetic surfactants in amounts up to 2000 $\mu g/\ell^{-1}$ to the solution studied did not affect the thickness of the surface microlayer sampled.

The results of the study lead to certain conclusions:

(1) The amount of sampled water, and hence the thickness of the sampled layer, are independent of the salinity of the water and presence of detergents.

(2) Independently of its own area, the screen sampler made of a nylon net with a mesh area of 1 mm^2 samples a water layer 220 microns thick with a variation coefficient of 4.4-10%.

In the winter of 1975-76, water samples were taken from the surface micro-layer in various regions of the Atlantic Ocean for the purpose of studying oil pollution. The results of an analysis of these samples by the "Oil-102" IR analyzer are presented in Table 4.

The highest concentrations of petroleum products in the water of the surface microlayer were found in the region of the Canary Islands. A little later they were found in studies in the region of 30°W. For comparison, let us note that at the 1-m level (the water was collected with Niskin's plastic sampler), trace amounts of petroleum products were detected, the maximum of which was only 0.3 mg/ℓ^{-1}.

TABLE 3. RESULTS OF DETERMINATION OF THE THICKNESS OF SAMPLED SURFACE MICROLAYER WITH A SCREEN SAMPLER MODEL HAVING A MESH AREA OF 1 mm^2 FOR WATER WITH ADDITIONS OF DETERGENTS

Type of sampler	n	Type and amount of detergent added, μg/ℓ	S	v	δ	K	CI	Z	$S^0/00$
Model of sampler with a mesh area of 1 mm^2	31	"Novost" - 1000	100	2.0	0.04	1.6	2.0=0.05	200	36,980
	38	Sodium alkylbenzoyl-sulfate - 1000	100	2.0	0.05	1.6	2.0=0.05	200	33,527
	39	"Novost" - 1000	100	2.0	0.05	1.5	2.0=0.05	200	distillate
	32	Sodium alkylbenzoyl-sulfate - 100	100	2.0	0.05	1.5	2.0=0.05	200	distillate
	47	"Novost" - 2000	100	2.0	0.05	1.5	2.0=0.05	200	36,980

Symbols:

n - number of determination

v - average amount of water collected at one time, cm^3

δ - rms deviation, cm^3

S - area of sampler, cm^2

K - variation coefficient, %

CI - confidence interval, cm^3

Z - thickness of sampled layer, microns

$S\ ^0/00$ - salinity of sample, $^0/00$

TABLE 4. COORDINATES OF STATIONS AND RESULTS OF DETERMINATION OF THE CONTENT OF PETROLEUM PRODUCTS IN THE SURFACE MICROLAYER OF SEAWATER IN THE WINTER OF 1975-76

Coordinates		Oil concentration, mg/ℓ^{-1}
(N)	(W)	
27°37	026°36	3,80
27°48	026°38	4,20
28°05	026°00	2,20
28°14	025°47	2,40
28°33	025°52	1,80
28°30	025°37	3,20
28°58	026°03	2,80
29°30	026°20	3,10
29°28	026°22	1,80
29°10	026°27	0,70
29°01	026°28	0,80
31°00	030°00	0,56
34°00	030°00	0,45
36°00	030°00	1,60
38°01	030°02	1,80
40°00	030°00	2,00
46°00	030°03	2,00
50°00	018°22	2,30
50°00	010°00	2,65

REFERENCES

1. Bol'shakov, V.S. 1968. Comparative Hydrological Characteristics of the Black, Azov, and Caspian Seas. Ecological Biogeography of Contact Marine Zones. Naukova Dumka, Kiev, 69 pp.

2. Balashov, A.I., Yu. P. Zaytsev, G.M. Kogan, and V.I. Mikhaylov. 1974. Study of Certain Components of the Chemical Composition of Water at the Ocean-atmosphere Boundary. Okeanologiya, Vol. 14, No. 5, pp. 817-821.

3. Kogan, G.M. 1969. Determination of Certain Trace Elements in Black Sea Water. Problems of Bioceanography. Naukova Dumka, Kiev, 127 pp.

4. Timoshchuk, V.N. 1970. Description of the "Afrodita-1" Device for Collecting the Neustic Water Layer. Radioecological Studies of the Mediterranean Sea. Naukova Dumka, Kiev, 87 pp.

5. Roll', G.U. 1968. Physics of Atmospheric Processes above the Sea. Gidrometeoizdat, 237 pp.

6. Tsyban', A.V. 1967. Nature of the Collection of Microbiological Samples in the Near-surface Microhorizon of the Sea. Gidrobiologicheskiy zhurnal, Vol. III, No. 2, pp. 47-52.

7. Skopintsev, B.A. 1938. Organic Matter in Seawater and Foam of the Southwestern Region of the Caspian Sea (Oct.-Dec. 1936). DAN SSSR, Vol. 18, No. 7, pp. 352-358.

8. Garrett, W.D., and W.R. Barber. 1974. Sampling and Determining the Concentration of Film-forming Organic Constituents of the Air-water Interface. Naval Research Laboratory Memorandum Report 2852, Washington, DC pp. 113-115.

9. Kanwisher, J. 1963. On the Exchange of Gases between the Atmosphere and the Sea. Deep-Sea Res., Vol. 10, 195 pp.

10. Horne, R.A. 1972. Structure of Seawater and its Role in Chemical Mass Transport between the Sea and the Atmosphere. J. Geophys. Res., Vol. 77, No. 27, pp. 5171-5176.

11. Harvey, G.W. 1969. Microlayer Collection from the Sea Surface. Limnol. Oceanographer, Vol. II, pp. 608-613.

12. McAlister, E.D., and W. McLeish. 1969. Heat Transport in the Top Millimeter of the Ocean. J. Geophys.. Res., Vol. 13, No. 74, pp. 217-225.

13. Zobell, C.E. 1939. Occurrence and Activity of Bacteria in Marine Sediments. In: Recent Marine Sediments, P.D. Trask, Ed., Am. Assoc. Petroleum Geologists, Tulsa, OK, pp. 87-95.

14. Ewing, G.C., and E.D. McAlister. 1960. On the Thermal Boundary Layer of the Ocean. Science, Vol. 13, No. 131, pp. 169-178.

15. Welander, P. 1959. Coupling between Sea and Air. Proceedings of Oceanogr. Congress, New York, pp. 67-71

CESIUM-137 AS A TRACER FOR REACTIVE POLLUTANTS IN ESTUARINE SEDIMENTS

H.J. Simpson, C.R. Olsen, R. Bopp, P.M. Bower, R.M. Trier, and S.C. Williams
Lamont-Doherty Geological Observatory
Palisades, NY 10964

ABSTRACT

Many reactive pollutants discharged to natural waters become associated with fine-grained particles. Accumulation and transport patterns of fine particles in estuaries and other natural water systems can be quite complex and difficult to predict. Cesium-137, a fission product with a 30-year half-life, has been added in readily measureable quantities to natural waters around the globe as a result of fallout from atmospheric nuclear weapons testing. Measurement of Cs-137 in estuarine sediments can be used to rapidly establish the distribution of recent (last two decades) fine-grained sediments. In the sediments of the Hudson River Estuary (USA), the amount of Cs-137 has been found to correlate with the distribution of a wide range of reactive pollutants in sediment depth profiles as well as in surface sediment concentrations. The pollutants for which we have found such a covariance with Cs-137 include Pu-239, 240, PCBs, Zn, Cu, Pb, Cd, and Ni.

INTRODUCTION

A substantial number of the pollutants discharged into natural waters can be classified as "reactive" in terms of their propensity to be associated with particles, either in the original effluent or after becoming dispersed in the receiving water. For example, metals from the electroplating industry and some types of artificial radionuclides released from nuclear power plants are transported and accumulated on particles in natural waters, as well as in solution. The particles most important in reactive pollutant transport are usually relatively small and often contain both organic and inorganic components. We will not discuss the composition or sorption characteristics of these fine particles, but instead will describe some of their characteristics as vectors of pollutant dispersal and accumulation.

---

*Present address: Lederle Laboratory, Pearl River, NY.

In estuaries, fine particles (<63 microns) are quite mobile and often undergo many episodes of deposition and resuspension by the variable currents of tidal waters. In theory, it should be possible to describe and predict the pathways of fine particle transport in estuaries, based on the physics of the particle motions and numerical models of sufficient complexity, or from properly scaled physical models. Actually, it is more practical to make direct field measurements of particle transport or to use tracers to infer the net motion of particles over extended periods of time. The approach described here uses a "natural" tracer (Cesium-137), which has become associated with fine particles in estuaries, as a guide to the distribution and transport of fine-grained sediments and several types of pollutants. The pattern of accumulation of fine particles in estuarine sediments is complex and essentially unique to each estuary. As a first approximation, estuarine sediments can be grouped into three end members: (1) large mineral particles, such as quartz sands, which are relatively unimportant in the transport of reactive pollutants; (2) fine particles (generally < 63 microns) which have not acquired significant quantities of pollutants, primarily because they have had relatively little contact with soluble phase pollutants; and (3) fine particles with readily measurable quantities of pollutants, which will be referred to here as "recent" fines. Obviously, the degree of contamination of recent fines can be extremely variable, but, as will be shown in the case of the Hudson River Estuary (USA), there is often a relatively uniform dispersal of reactive pollutants in recent fine particles over large areas and a surprisingly coherent distribution of several types of pollutants.

CESIUM-137 AS AN INDICATOR OF RECENT SEDIMENTS

Atmospheric testing of large nuclear weapons during the 1950's and early 1960's, predominantly by the USA and USSR, dispersed a great variety of radionuclides over the entire earth. A number of these nuclides have sufficiently long radioactive half-lives to be valuable as tracers of global scale processes. The pattern and time scale of deposition of Strontium-90 ($t_{1/2} \sim 29$ years), especially in the Northern Hemisphere, have been followed closely (15, 16) because of its long half-life, potentially serious biological impact, and the existence of relatively direct pathways by which this nuclide can reach man. The depositional history of Cs-137 ($t_{1/2} \sim 30$ years) has not been documented as well as Sr-90 because it does not appear to be of nearly as much biological concern to man as Sr-90. Available data indicate that the pattern of delivery of atmospheric fallout Cs-137 to the earth's surface can be assumed to be identical to Sr-90, with an activity ratio of Cs-137 to Sr-90 of ~ 1.5 (9, 7). The peak delivery of fallout Cs-137 to the earth's surface by rain and snow occurred during the years 1962 to 1964; the quantities deposited since then have been relatively small. Most of the Sr-90 (and Cs-137) fallout on land has been retained in the upper 10 to 20 cm of the soil profile and the total activity present per unit area is proportional to the annual rainfall (8) as well as being a function of the latitude (15).

In the open ocean, both Sr-90 and Cs-137 appear to have remained predominantly in solution (3, 6, 1), although there is some indication of preferential removal of Cs-137 into the sediments (10). The fraction of total fallout Cs-137 delivered to the ocean which is now in the sediments is quite small.

In most freshwater lakes, Sr-90 stays in solution to the first approximation, but Cs-137 is nearly completely removed onto particles (17, 5). In rivers and estuaries, the fraction of fallout Cs-137 associated with sediment particles (compared with that which passed through these systems in solution) is not well-defined (11), but readily measurable amounts are found in the sediments of estuaries which we have studied.

We usually measure Cs-137 in estuarine sediments by gamma counting 50 to 100 gram samples of dried sediment which have undergone no chemical steps to enrich the specific activity of the samples. Our counting equipment consists of a high resolution lithium-drifted germanium detector and a multichannel analyzer, which allows us to simultaneously measure the activity of many other radionuclides (both natural and artificial) as well as the Cs-137 gamma emission peak at 662 Kev. Because of our ability to measure Cs-137 at "normal" environmental levels in sediments with non-destructive gamma counting, we are able to process a large number of samples with relatively little effort in laboratory preparation, compared with the analytical techniques required for most pollutant measurements. The detection limit for most of our samples was 10 to 20 pCi/kg, which is a few per cent of the activity typical of surface soils in the Northern Hemisphere.

CESIUM-137 AND OTHER ANTHROPOGENIC COMPONENTS IN HUDSON ESTUARY SEDIMENTS

The total delivery of fallout Cs-137 to the Hudson Estuary, decay corrected to 1975, has been about 120 mCi/km^2 (U.S. ERDA, 1975). There is an additional supply of Cs-137 from a nuclear electrical-generating facility located near the upstream end of the salinity intrusion in the Hudson. The total release of Cs-137 from this facility over more than a decade of operation has been comparable to the amount supplied by rain to the surface of the Hudson Estuary from global fallout. Thus the direct supply of Cs-137 to the Hudson Estuary is roughly a factor of two greater than might be expected if fallout were the only source.

The specific activity of Cs-137 in surface sediments in the Hudson ranges over more than two orders of magnitude, with the lowest values in sandy sediments (typical of areas scoured of fine particles by strong currents). Fine-grained surface sediments ($< 63\ \mu$) usually range between 0.2 and 2 pCi/g of Cs-137, which is comparable to fallout Cs-137 activity in surface soils throughout the Northern Hemisphere (7, 12). There is large variation in the depth to which Cs-137 is found in sediment cores. In most areas Cs-137 activity is confined to the upper 5 cm of the sediment column, whereas in others it extends to nearly 3 meters below the sediment surface. Thus the integrated amount of Cs-137 per unit sediment area is not uniform, and ranges over more than two orders of magnitude. As a result, relatively limited geographical areas account for large portions of the total sediment burden of Cs-137. In the Hudson Estuary (Fig. 1), the dominant areas of Cs-137 accumulation are the harbor and shallow coves upstream of the harbor. These areas are not in close proximity to the site of localized discharge of CS-137 to the Hudson, and primarily reflect the zones in which fine particles are rapidly accumulating (13).

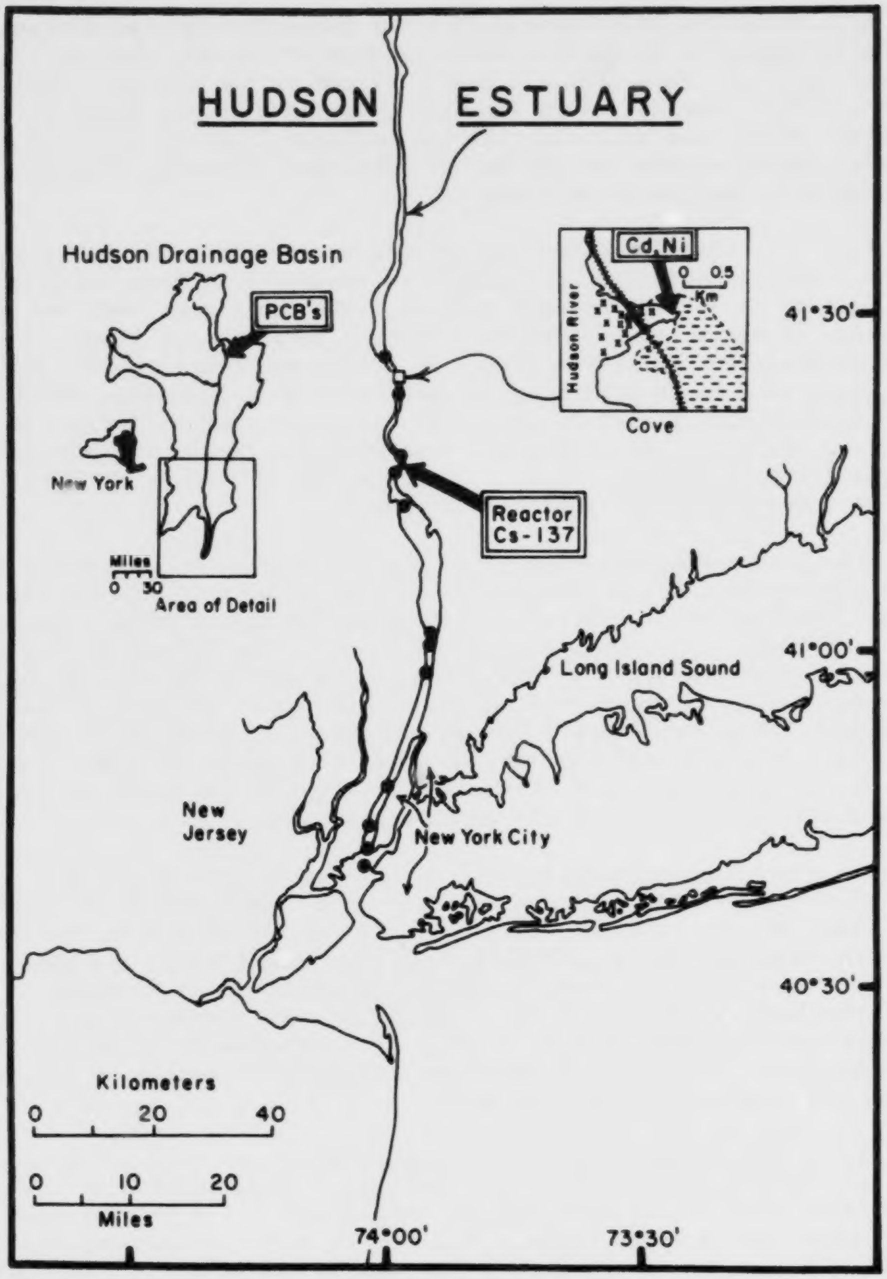


Figure 1. Locations of cores for which data are reported in this paper are indicated by ⊗. The most-northerly sampling sites are near the upstream limit of saltwater intrusion of the Hudson Estuary during summer months, and the harbor sites adjacent to New York City usually have salinities of one half to two thirds that of seawater. The Hudson is tidal for approximately 250 km upstream of New York City. The locations of discharge of polychlorinated biphenyls (PCBs), cadmium and Nickel (Cd, Ni), and radioactive cesium (Cs-137) are also indicated.

We have found the distribution of other man-made reactive contaminants in Hudson sediments to be quite similar to that of Cs-137, despite significant differences in chemistry, and mode of input to the system. The locations of sediment sampling sites for data reported here are shown in Fig. 1. These sites extend from approximately the upstream limit of salinity intrusion during summer months to the harbor area that typically has salinities of approximately two-thirds of seawater.

In Fig. 2, activities of Pu-239,240, determined by alpha spectrometry following chemical separation procedures as described by Wong (18), are plotted against Cs-137 in the same samples. The covariance over two orders of magnitude of these two parameters in Hudson sediments is clear. Thus if the present distribution of Pu-239,240 in Hudson sediments (mostly derived from fallout) were to be measured, the most efficient procedure would be to use the distribution of Cs-137, which is relatively easy to measure by gamma spectrometry, to guide the selection of samples for Pu-239,240 analysis. (The alpha particle energies of Pu-239 and Pu-240 are nearly identical and the sum of their activities is usually reported.)

In Fig. 3, the concentration of polychlorinated biphenyls (PCBs) in Hudson sediments is plotted against Cs-137. Although our data are limited at this time, the covariance of these constituents is also obvious. The levels of PCBs are high in sediments over large areas of the Hudson because of industrial releases during the 1950's and 1960's at two sites more than 200 km upstream from the locations of our sampling area. Considering the great differences in chemistry between Cs-137 and PCBs, it is perhaps surprising to find their sediment distributions to be as similar as they are, but their covariance is a good indicator of the ability of fine particles to transport and accumulate quite a variety of reactive pollutants.

Fig. 4 shows the concentration of several trace metals relative to Cs-137. Zinc, copper, and lead concentrations in recent Hudson sediments are several times the concentration levels in pre-industrial sediments. All of the samples shown in Fig. 4 are upstream of the harbor area, and thus reflect diffuse sources of these metals to the Hudson over a number of decades. Sediment samples from New York Harbor have somewhat higher concentrations for all three metals, because of discharges from the electroplating industry. Vertical distributions of all three metals in harbor sediments also are similar to that of Cs-137.

In Fig. 5 the concentrations of cadmium and nickel in a small cove are plotted against Cs-137 activity. High level contamination of the sediments of this small ($\sim$ 0.5 km^2) shallow (mean depth $\sim$ 1-2 meters) area by effluent from a battery factory has resulted in Cd concentrations ranging from a few per cent to $\sim$100 ppm (2). Some surface sediments in the cove which are apparently in areas of active current scouring contain relatively low concentrations of Cd, Ni, and Cs-137. Thus Cs-137 is useful in mapping the pattern of trace metal accumulation in sediments in relatively small, highly contaminated areas, as well as for diffuse sources over large areas.

All of the "reactive" pollutants we measured in Hudson Estuary sediments are found preferentially in fine particles and in sediments rich in organic

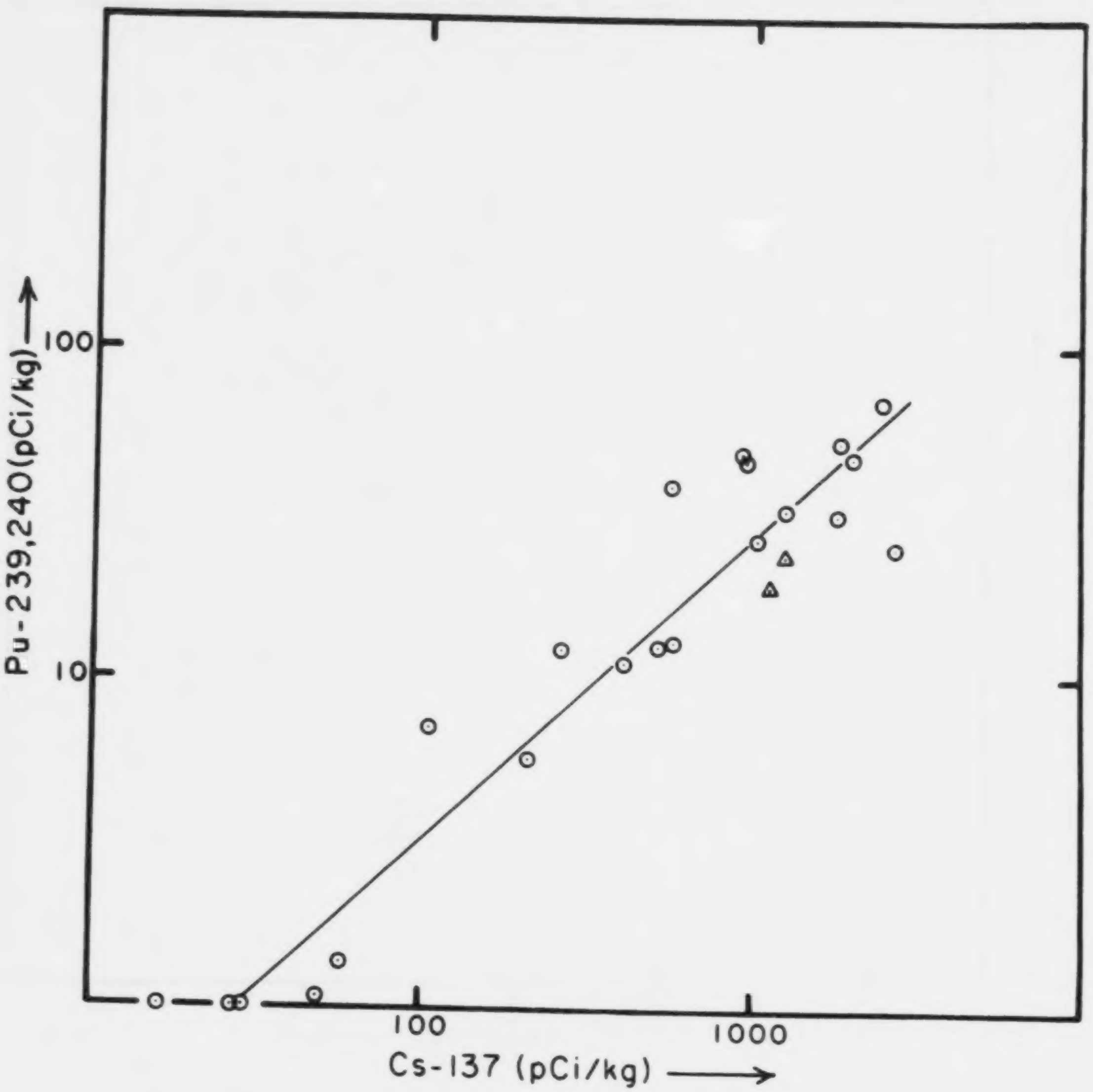


Figure 2. Activities of Cs-137 and Pu-239,240 in Hudson Estuary sediment. Samples are given for sites indicated in Fig. 1. Data are for samples well below the sediment-water interface, as well as surface sediment samples. Two suspended particulate samples (Δ) collected near the middle of the sampling range are also included. All data are expressed as activity per dry weight of sediment.

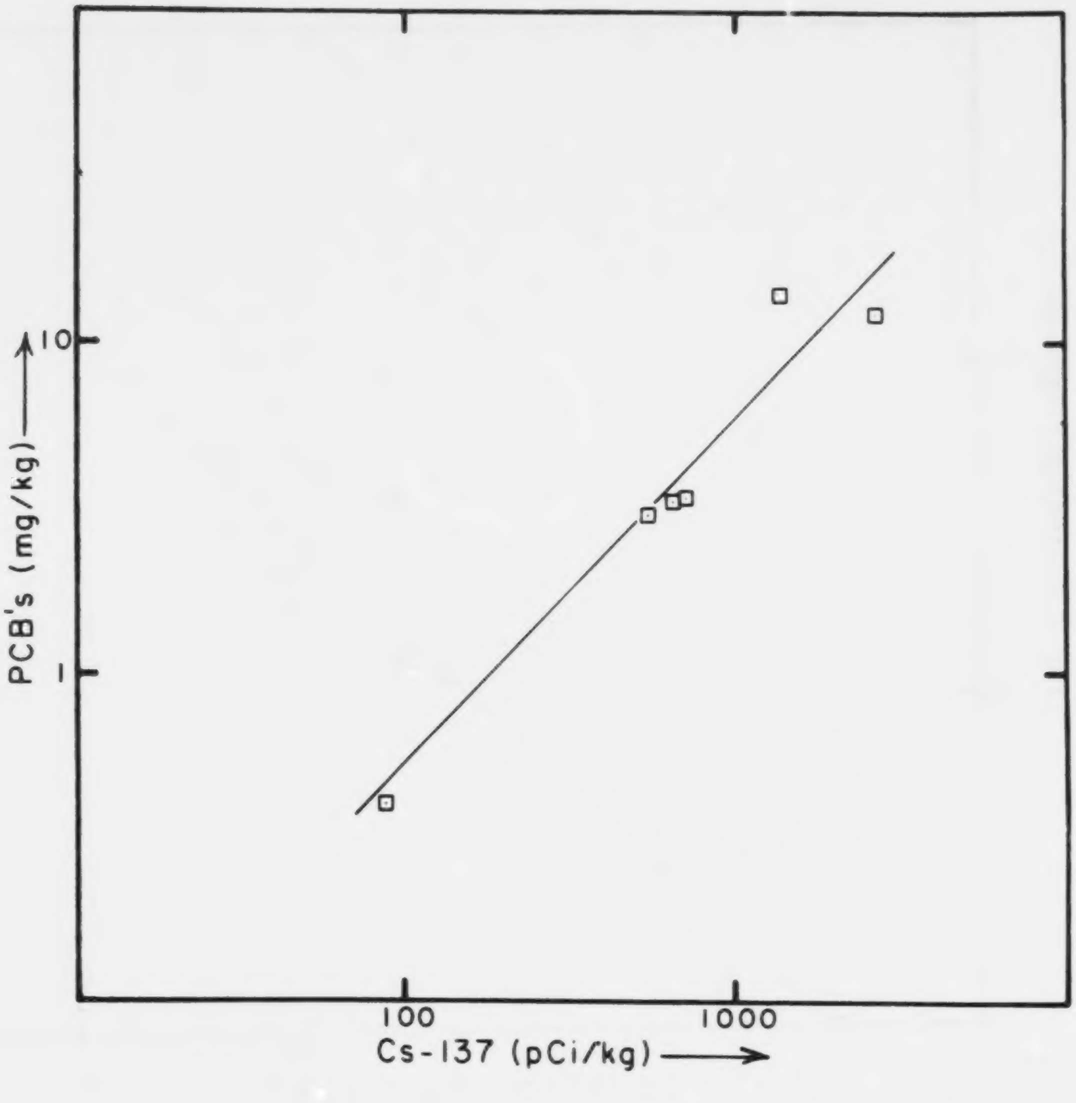


Figure 3. Activities of Cs-137 and concentrations of polychlorinated biphenyls (PCBs) in samples of surface sediment are given for Hudson Estuary sites included in Fig. 1. All data are expressed in terms of dry weight. PCBs were soxhlet-extracted from the sediments, by azeotropic hexane acetone and quantified by electron capture gas chromatography.

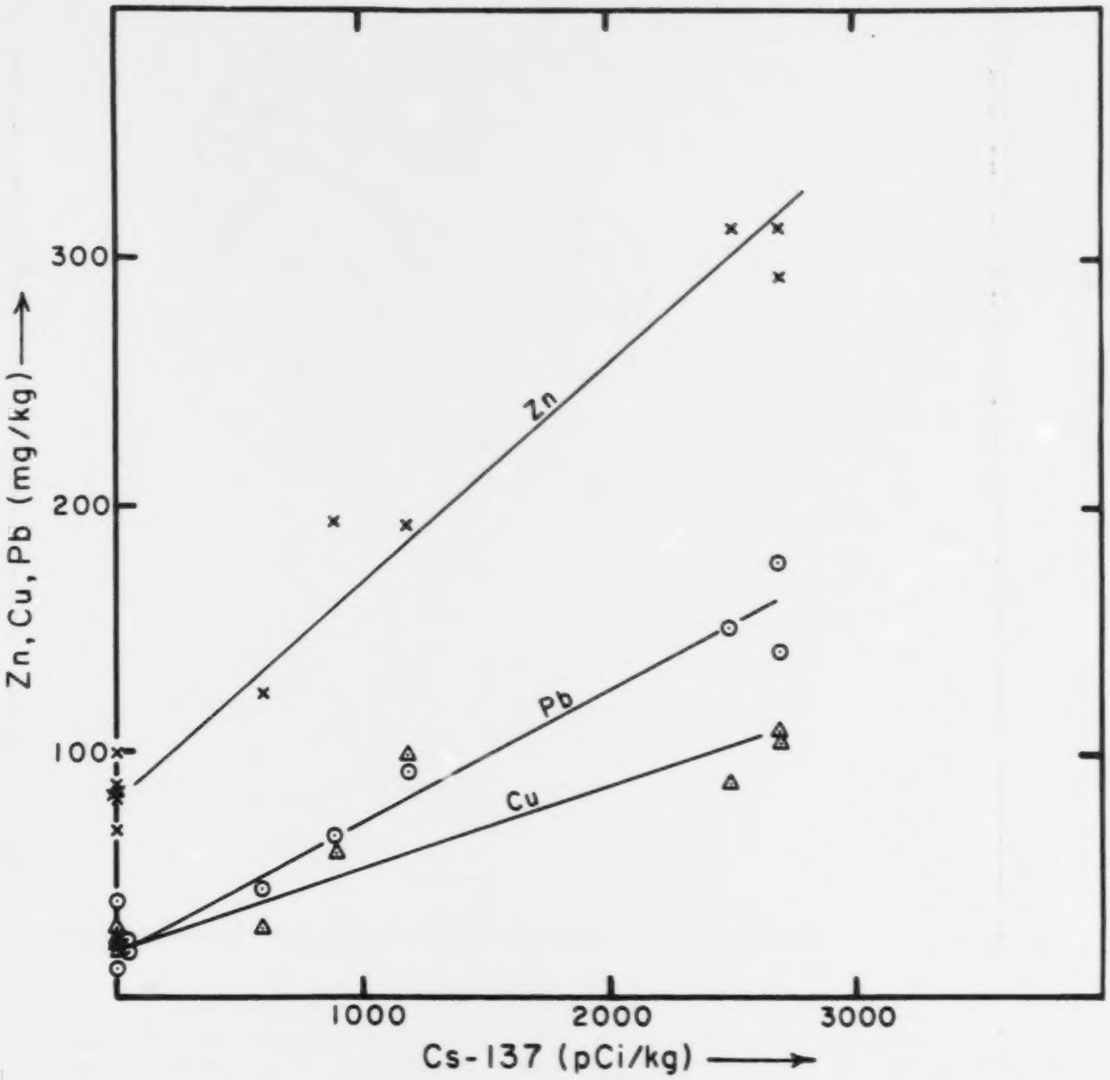


Figure 4. Activities of Cs-137 and concentrations of zinc (X), copper (Δ), and lead (⊙) in Hudson Estuary sediment samples are plotted for sites indicated in Fig. 1. Data are for samples well below the sediment-water interface as well as surface sediment samples. The data are presented on a linear plot to indicate the observed range of pre-industrial concentrations in Hudson sediments on the Y axis. All data are expressed in terms of dry weight. All trace metal data reported here were obtained by flame atomic absorption spectrometry.

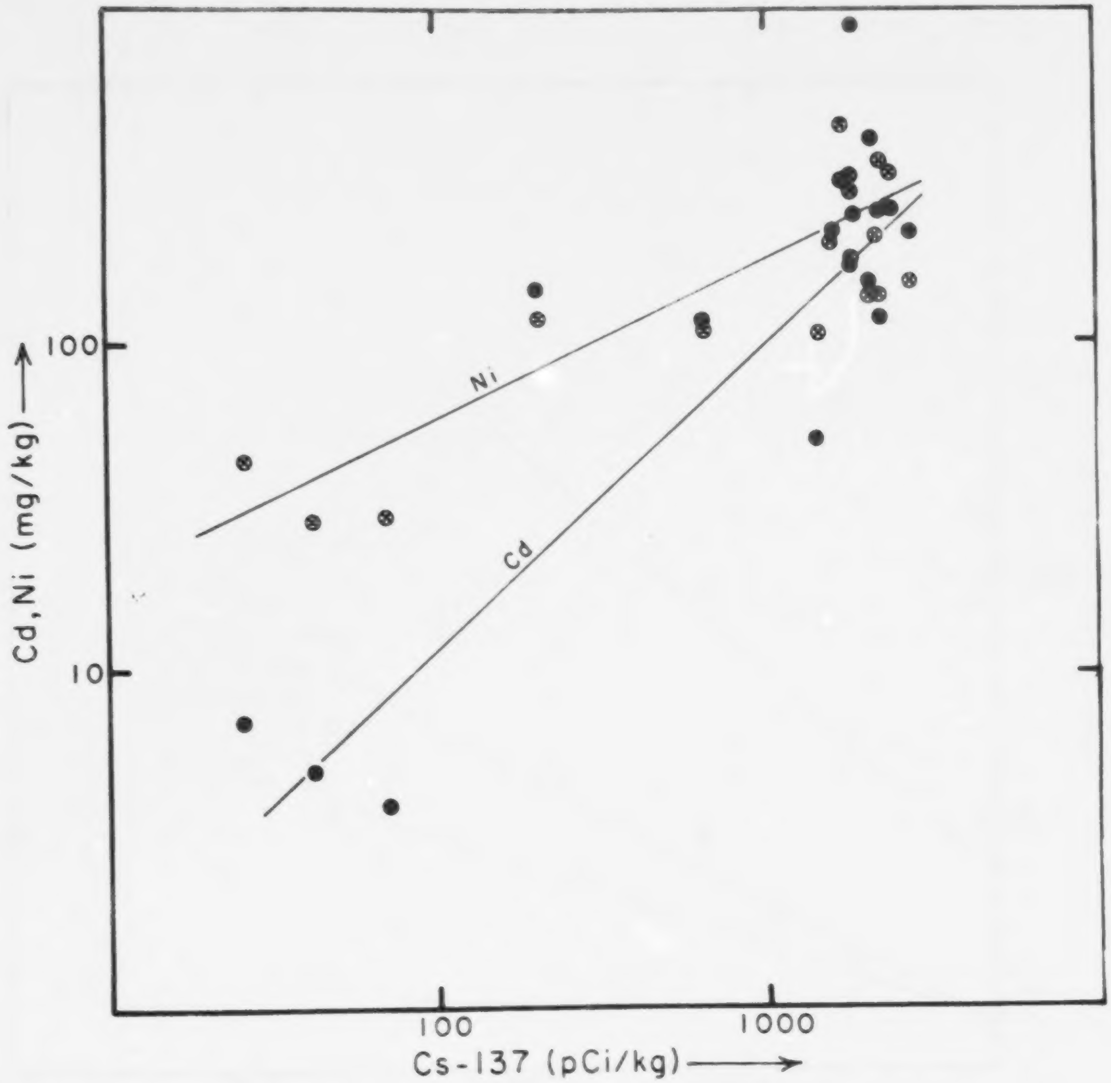


Figure 5. Activities of Cs-137 and concentrations of cadmium (●) and nickel (⊗) are given for sediment samples from a small cove in the Hudson receiving effluent from a battery factory (see insert in Fig. 1 where locations of samples are indicated by ⊗'s). Some of the lowest concentrations are from surface samples of fine-grained sediment in areas which are apparently scoured by tidal currents and are thus kept free of recently deposited sediments. Samples from these scoured sites have a similar physical appearance to those from the highly contaminated sites. The trend lines drawn for Cd and Ni are not fitted mathematically, and do not imply a linear relationship between Cd, Ni and Cs-137 on a log-log plot. The lines are included primarily to indicate that samples in this highly contaminated cove which have low activities of Cs-137, also have relatively little Cd and Ni concentration. The background concentrations of Ni are more than an order of magnitude higher than for Cd, which causes the slopes of the two trend lines to differ significantly.

matter, as would be expected. However, many sediment samples with very similar particle size distributions and organic carbon contents did not have appreciable reactive pollutant concentrations (and they did not have measurable Cs-137). Thus the activity of Cs-137 was a much more accurate indicator of probable pollutant concentration than were classical sedimentological techniques, especially in estimating the depth to which appreciable pollutant concentrations would be found in estuary sediment cores.

CESIUM-137 AS A POLLUTANT TRACER IN OTHER AQUEOUS SYSTEMS

Fallout Cs-137 has been used as an indicator of recent sediments in the Delaware Estuary. Sites with appreciable activity of Cs-137 in surface sediments also have hydrocarbon constituents typical of recent pollution, whereas surface sediments free of Cs-137 has been shown to be nonuniform in large lakes and to be closely related to that of fallout Pu-239,240 (4).

The concentration of a number of reactive pollutants in Hudson Estuary sediments, although extremely variable in both surface and depth distributions, has been shown to have considerable coherence from one pollutant to another and to have a strong correlation with Cs-137. Thus the task of mapping contaminated sediment distributions in complicated sedimentary regimes can be simplified through the use of a "natural" tracer, Cs-137.

ACKNOWLEDGEMENTS

Financial support for the research reported here was provided by the U. S. Environmental Protection Agency (R803113) and the U. S. Energy Research and Development Administration (E (11-1) 2529). Contribution No. 2479 from Lamont-Doherty Geological Observatory of Columbia University.

REFERENCES

1. Bowen, V.T., and W. Roether. 1973. Vertical Distributions of Strontium-90, Cesium-137, and Tritium near 45° North in the Atlantic, J. Geophys. Res., 78, pp. 6277-6285.

2. Bower, P.M. 1976. Burdens of Industrial Cadmium and Nickel in the Sediments of Doundry Cove, Cold Spring, New York. M.S. Thesis, Queens College of the City University of New York, 162 pp.

3. Broecker, W.S., E.R. Bonebakker, and G.G. Rocco. The Vertical Distribution of Cesium-137 and Strontium-90 in the Oceans, 2, J. Geophys. Res., 71, pp. 199-2003.

4. Edgington, D.N., J.J. Alberts, M.A. Wahlgren, J. O. Karttunen, and C.A. Reeve. 1976. Plutonium and Americium in Lake Michigan Sediments, Transuranium Nuclides in the Environment, IAEA-SM-199/47, IAEA, Vienna, pp. 493-516.

5. Farmer, J.G., V.T. Bowen, and V.E. Noshkin. 1977. Long-lived Artificial Radionuclides in Lake Ontario, I. Supply from Fallout, and Concentrations in Lake Water of Plutonium, Americium, Strontium-90 and Cesium-137. (Submitted to Limnology and Oceanography.)

6. Folsom, T.R., C. Sreekumaran, N. Hansen, J.M. Moore, and R. Grismore. 1970. Some Concentrations of Cs-137 at Moderate Depths in the Pacific 1965-1968. U. S. Atomic Energy Commission (AEC) Rep. HASL-217, pp. 1-9.

7. Hardy, E.P. 1974. Depth Distributions of Global Fallout Sr-90, Cs-137, and Pu-239,240 in Sandy Loam Soil. U. S. AEC Rep. HASL-217, pp. 1-9.

8. Hardy, E.P., and L.T. Alexander. 1962. Rainfall and Deposition of Sr-90 in Clallam County, Washington. Science, 136, pp. 881-882.

9. Harley, N., I. Fisenne, L.D.Y. Ong, and J. Harley. 1965. Fission Yield and Fission Product Decay. U. S. AEC Rep. HASL-164.

10. Noshkin, V.E., and V.T. Bowen. 1973. Concentrations and Distributions of Long-lived Fallout Radionuclides in Open Ocean Sediments, Radioactive Contamination of the Marine Environment. IAEA, Vienna, pp. 671-686.

11. Riel, G.K. 1972. The Distribution of Fallout Cesium-137 in the Chesapeake Bay. Proceedings of the Second International Symposium on the Natural Radiation Environment, J.A.S. Adams, W.M. Lowder, T.F. Gesell, eds. pp. 883-896.

12. Ritchie, J.C., P.H. Hawks, and J.R. McHenry. 1975. Deposition Rates in Valleys Determined Using Fallout Cesium-137. Geol. Soc. Amer. Bull., 86, pp. 1128-1130.

13. Simpson, H.J., C.R. Olsen, R.M. Trier, and S.C. Williams. 1976. Man-made Radionuclides and Sedimentation in the Hudson River Estuary. Science, 194, pp. 179-183.

14. U. S. Energy Research and Deveopment Administration (ERDA) Rep. HASL-294 1975, appendix, pp. 68-70.

15. Volchok, H.L. 1966. The Global Strontium-90 Budget, J. Geophys. Res., 71, pp. 1515-1518.

16. Volchok, H.L., and M.T. Kleinman. 1971. Global Sr-90 Fallout and Precipitation: Summary of the Data by 10 Degree Bands of Latitude, U.S. AEC Rep. HASL-245, pp. 2-83.

17. Wahlgren, M.A., and J.S. Marshall. 1975. The Behavior of Plutonium and Other Long-lived Radionuclides in Lake Michigan: I. Biological Transport, Seasonal Cycling and Residence Times in the Water Column, International Symposium on Transuranium Nuclides in the Environment. IAEA-SM-198/39, IAEA, Vienna, pp. 227.

18. Wong, K.M. 1971. Radiochemical Determination of Plutonium in Seawater, Sediments, and Organisms. Anal. Chim. Acta, 56, pp. 355-364.

THE DISTRIBUTION OF POLLUTANTS IN THE CARIBBEAN BASIN

M.M. Domanov, B.A. Nelepo, and V.N. Stepanov
P.P. Shershov Oceanology Institute, U.S.S.R. Academy of Sciences

The authors of this paper took part in the research work conducted during recent years in the Caribbean Sea and the Gulf of Mexico under the auspices of United Nations Education, Scientific, and Cultural Organization (UNESCO). The hydrographical investigations, conducted in 1973 on board the r/v Akademik Kurchatov, confirm the general statement that oil and chemical pollution is increasing, while the danger of radioactive contamination shows a decrease.

OIL POLLUTION

Large spots and streaks of oil were encountered everywhere along our route. Most pollution was found in the waters of the Caribbean Sea and the Gulf of Mexico. The strong, steady Caribbean current carries the oil emitted by tankers in the central part of the Caribbean Sea (from the Lesser Antilles to the Yucatán Channel).

In the northern part of the Caribbean Sea, where according to our investigations an anticyclonic circulation prevails, oil products will accumulate in the central parts of such gyres (Fig. 1) situated near the Great Antilles. In the southern part of the sea, a rather intensive cyclonic circulation was discovered. Thus, oil will be carried to the margins of these systems, polluting the coasts of Colombia and Venezuella.

In the Gulf of Mexico, the main mass of oil entering through the Yucatán Channel will be carried away to the coasts of Cuba and Florida and thereafter through the Florida Straits into the open ocean. In the western part of the Gulf, the pollutants will spread from north to south along the coasts, and accumulate in open aquatories in the separate closed gyres situated in this region.

Our plankton nets brought up great quantities of small lumps of black oil, varying in size from a poppy seed to several centimeters in diameter. Small animals, cirripeds, actinians, and hydroids are frequently found attached to their surfaces. Larger pieces have small-hole refuges made by tiny crustaceans. This circumstance cannot avoid affecting the biological resources of the world's oceans, as plankton forms the basis of the aquatic food chain. The adverse effect exercised by oil pollution on phytoplankton may lead to a decrease in oxygen production by marine algae. If this gas is generated by the life activity of plants on our planet, the share demanded by phytoplankton of planetary oxygen must be very substantial.

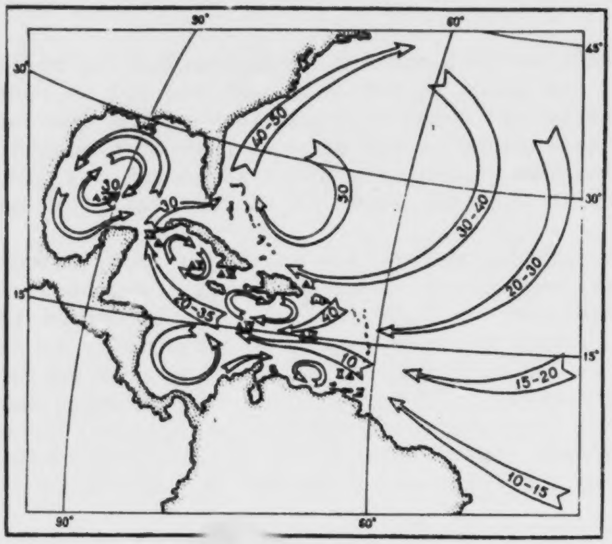


Figure 1. The scheme of [illegible] distribution of the radioactive pollution. Concentration of the strontium-90 in disintegrations per minute in 100 m of the water according to the available data. Sites measured are marked by Roman numerals.

TOXIC CHEMICALS IN THE OCEAN

The Mexican oceanographers who stayed for some time aboard the Akademik Kurchatov told us about heavy pollution of seawater by chemical fertilizers carried into the ocean with river discharge. Special investigations are conducted to determine the content of DDT and other pesticides in the bodies of fish and crustaceans. These chemicals tend to accumulate in great quantities in the tissues of living organisms and are not easily eliminated. In human organisms, they penetrate with ingested contaminated seafood.

Such investigations are of special importance to the western part of the Gulf of Mexico, into which the Mississippi River empties. The waters of this river, the greatest on our planet, flow through 31 states enroute to the sea and carry a heavy load of toxic chemicals. They spread along the western and southern coasts of Mexico and are carried by the Florida current into the open ocean.

ARTIFICIAL RADIOACTIVITY IN THE CARIBBEAN BASIN

The investigations conducted aboard the Akademik Kurchatov yielded some information on the changes with depth in the content of radionuclides of artificial origin. The investigations were conducted at separate polygons confined to the deep sea depressions (trenches) of the Caribbean Basin and the Cayman Trough (Fig. 1). For comparison with oceanic conditions, one of the polygons was confined to the Puerto Rican Trough situated northward of Puerto Rico. The concentration of cesium-137 was determined by means of ion-exchange resins sunk at different distances between the surface and the bottom. Determinations were made of the nature and intensity of atmospheric radioactive fallouts.

The data obtained show that maximum concentrations of radionuclides occur, not at the surface of the ocean as believed earlier, but at depth of about 200 m. A direct relation was found to exist between the changes in depth and the concentration of radioisotopes and general physico-chemical stratification of the waters. The maximum concentrations of radionuclides discovered in the subsurface layer coincide with the layer of extreme salinity values.*

The concentration of cesium-137, low at the surface, increases rapidly with depth, reaches its maximum value in the lower layer of surface waters, and decreases gradually down to 100 m (Fig. 2). An exception is the profile obtained in the Gulf of Mexico where maximum radioactivity is found at the surface. This seems to be accounted for by the ascent of subsurface waters coming from the Caribbean Sea. If the analogy with salinity holds through the whole water column, then the concentration of radionuclides may be expected to show a certain increase toward the bottom, following the minimum values observed at the core of the intermediate waters and extending down to 800 to 1000 m.

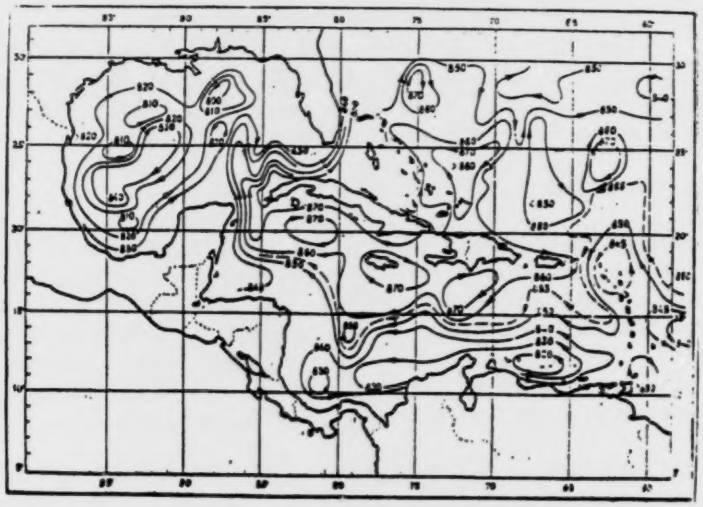


Figure 2. The water circulation on the surface from the reference level of the 2500 m.

The only possible local source of pollution could be the U. S. atomic industry. If uranium fissure products were released, then higher concentrations of strontium and cesium would be recorded in the Gulf of Mexico and in the Florida Straits where waters are carried into the open ocean. But available data show that the concentrations here are of the same order as those in the Caribbean Sea. Consequently, radionuclides of artificial origin must be carried in from the open part of the Atlantic Ocean.

---

*The surface waters are divided into three layers. The upper homogeneous layer has an average thickness of 20-50 m. The lower, or subsurface layer, is situated in depths varying from 50-100 to 250-300 m. They are separated by a relatively thin transition layer.

Considering the intensive transport of oceanic waters through the Caribbean basin, the above assumption is highly plausible. To make certain, we analyzed the data on strontium-90 concentration in the surface waters of the northern Atlantic, published by the U.S. HASL (1968). The data permitted us to establish a prevailing importance of strontium-90 in currents capable of transporting radioisotopes to the Caribbean Sea (Fig. 1). Corresponding concentrations were discovered in adjacent areas of the Caribbean Sea: the low values observed in the south and southeast increased to 40 to 50 dec/100ℓ/min at the Antilles Straits.

How are the high concentrations of radio-isotopes found in the lower layer of surface waters formed? The explanation apparently lies in the fact that surface water is drawn to the depths in the central regions of anticyclonic microcirculation systems and zones of convergence. The sunken waters begin to shift in the subsurface layer in a horizontal direction. In the Caribbean basin, judging from the relation between maximum radioisotope concentration and extreme salinity value, sinking of surface water in the open ocean is a most important factor in the western part of the subtropical anticyclonic macrocirculation. It is precisely at this point that the highest concentrations of radio-active substances are recorded (Fig. 1).

Owing to extensive descending movements, intermediate and deep-water masses are formed in the North Atlantic Ocean where the radioisotopes are carried into greater depths with the sinking surface waters. However, considering the immense volumes of the water masses involved, the concentrations cannot be of any substantial importance. On the other hand, the water mass in the subsurface layer is immeasurably smaller, and conditions there are favorable for the accumulation of uranium decay products. These processes are responsible for the changes with depth in the content of radioactive substances observed in the lower latitudes of the northern Atlantic and in the Caribbean Basin.

In areas where ascending movements generated in cyclonic macrocirculation systems and zones of divergence prevail, radionuclides carried previously to the depths may begin to shift upwards toward the ocean surface. In this way, in conformity with the patterns of vertical circulation, the exchange of substances concentrated in the world's oceans is achieved.

In addition to being transported, a local vertical exchange of radioactive products must take place in the Caribbean basin. In the northern part of the sea, in conformity with the peculiarities of its circulation, the radioisotopes will be carried down by the descending water movements generated by anticyclonic gyres (Fig. 3). Whereas in its southern part where cyclonic circulation prevails, the radioactivity at the surface will be increased by the decay products brought up from the subsurface layer.

In the Gulf of Mexico, under conditions of an extremely complex circulation, including numerous local rises and sinkings of water masses, the radioactivity field will display a great diversity of changes in concentration and stratification. On the whole, however, a transport of radionuclides to the surface may be expected. This has been discovered to be the case at polygon VI, the Gulf of Mexico.

Reproduced from
best available copy.

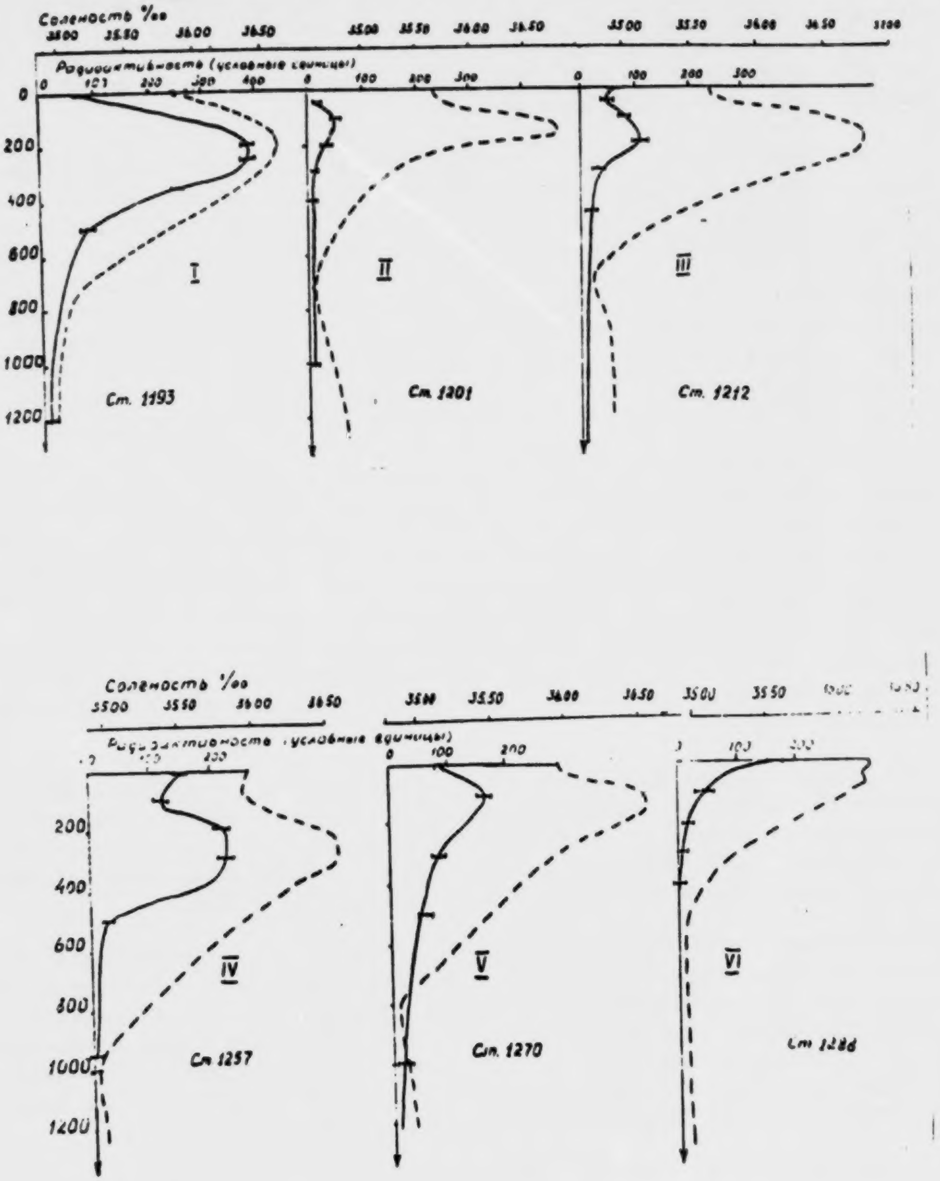


Figure 3. The vertical distribution of the cesium-137 (unbroken line) and salinity (broken line) by the data of the Academic Kurschatov expedition in the 1974 year.

An estimate was made of the balance of radioactive substances in the Caribbean Basin from data on radioisotope concentration and water exchange through the Antilles Straits. In order to convert the conventional radioactivity units into absolute units, the concentrations of strontium-90 at the surface of the ocean published by the U.S. HASL (1968) were compared with the values obtained by the isotope-exchange methods. As the conventional units of this method agree, within the measurements precision, with the absolute values of cesium-137 expressed in disintegrations per 100ℓ per minute, the same relationship also may be assumed to hold for other radionuclides (Table 1). A substantial difference was discovered only at polygon VI in the Gulf of Mexico, which, as stated above, was caused by an increase in concentration associated with the ascention of subsurface waters.

TABLE 1. COMPARISON OF RADIOISOTOPE CONCENTRATIONS IN CONDITIONAL AND ABSOLUTE UNITS

Region of dimension	Concentrations of radionucleids		
	Conditional units according to "Akademik Kurchatov"	Absolute units disintegration/100 litres/min according to HASL	
	Cs^{137}	Cs^{137}	Sr^{90}
Florida Strait	98	85	50
The Lesser Antilles Straits	13	17	10
Venezuela Basin	60	61	36
Westward Passage	88	85	50
Mona Passage	68	68	40
Gulf of Mexico	161	49	29

Calculations of the stock radiocesium (Table 2) show that the oceanic waters flowing in from the north carry 10 times more cesium-137 than waters coming from the equatorial zone. The high concentrations observed at polygons IV and V are apparently caused by an inflow of water from subtropical regions through the Windward and Mona Passages. As the radiocesium concentrations at these polygons are rather similar, it may be assumed that the same amounts of radionuclides are transported from the Caribbean Sea into the Gulf of Mexico, and, further, through the Florida Straits into the open ocean again.

Proceeding from the stock of radiocesium, the value of water inflow through the Antilles Straits, and assuming that the main mass of radionuclides is transported in the upper 1000 m layer, it is possible to calculate the quantities transported through the channel. The results of our computations are presented in Table 3. Owing to the lack of direct measurements for the Florida Straits, we used the relation between the changes with depth in salinity and radioactivity. The total value of the stock of radioisotopes in the

TABLE 2. RADIOISOTOPES CONTENT IN THE 0-1000 m LAYER*

Region of observations	Radioisotopes content				
	Conventional units	Disintegration ($km^3 min \times 10^7$)		Curies ($km^3 10^{-3}$)	
	Cs^{137}	Cs^{137}	Sr^{90}	Cs^{137}	Sr^{90}
Puerto-Rico Trough (polygon I)	70.5	70.5	41.4	3.17	1.86
Anegada Passage	21.2	21.2	12.4	0.95	0.56
Grenada Trough (polygon 2)	6.5	6.5	3.8	0.29	0.17
Venezuela (polygon 3)	13.7	13.7	8.1	0.62	0.36
Windward Passage	76	76	44.1	3.42	2.0
The Bartlett Deep of the Cayman Trough (polygon 5)	37	37	21.8	1.66	0.98
The Orient Deep of the Cayman Trough (polygon 5)	36.4	36.4	21.4	1.64	0.96
Gulf of Mexico (polygon 6)	5.8	5.8	3.3	0.26	0.15

*According to the Akademik Kurchatov expendition.

TABLE 3. WATER AND RADIONUCLIDE TRANSPORT IN THE UPPER 1000-M LAYER OF THE AMERICAN MEDITERRANEAN

Straits	Stock of radionuclides disintegrated km^3/min.x10^7		Inflow			Outflow		
			Water Volume km^3/sec.x x10^{-3}	Radionuclides disintegrated min.x10^7		Water volume km^3/sec.x x10^{-3}	Radionuclides disintegrated min.x10^7	
	Sr^{90}	Cs^{137}		Sr^{90}	Cs^{137}		Sr^{90}	Cs^{137}
Florida	21.8	37	0.7	15.2	25.8	26	565	962
Windward	44.7	76	12.7	565	965	4	178	302
Mona	41.4	70.5	1.9	78.5	134	0.3	12.5	21.2
Anegada	12.4	21.2	2.3	28.6	49	4.7	58.3	99.5
Lesser Antilles	3.7	6.3	17.4	64.5	110	-	-	-
			Total inflow			Total outflow		
			35	751.8	1283.8	35	813.8	1384.7
				$3.48 \cdot 10^{-3}$	$5.8 \cdot 10^{-3}$		$3.66 \cdot 10^{-3}$	$6.23 \cdot 10^{-3}$
				curies	curies		curies	curies

0 to 1000-m layer is assumed to be the same as that of Polygon IV.

The value of the stock of radiocesium in the waters flowing in through the Windward and Anagada Passages (instrumental measurements for cesium-137 are not available) are derived from the equation of radionuclide balance; an estimate was made of the total quantities brought into the Caribbean Sea through the Antilles Straits and carried out into the ocean through the Straits of Florida (Table 3). A certain excess of outflow over inflow is probably due to underestimating the quantity of radioisotopes carried away by the intermediate waters.

As compared with the level of radioactive pollution in European seawater, the values recorded in the Caribbean Basin are relatively low. This evidence supports our assumption that radioactive contamination in the Caribbean Basin depends not on the release of nuclear wastes by local atomic industry, but on the general level of contamination in the ocean as a whole. We have here an illustration of the role of global pollution in the destiny of individual regions. It becomes increasingly evident that it is practically impossible to solve the problem by local efforts.

Most important in preventing pollution and poisoning of the world's oceans is the cooperation of the general public. It is in this light that the data collected by the *Akademik Kurchatov* present a certain interest.

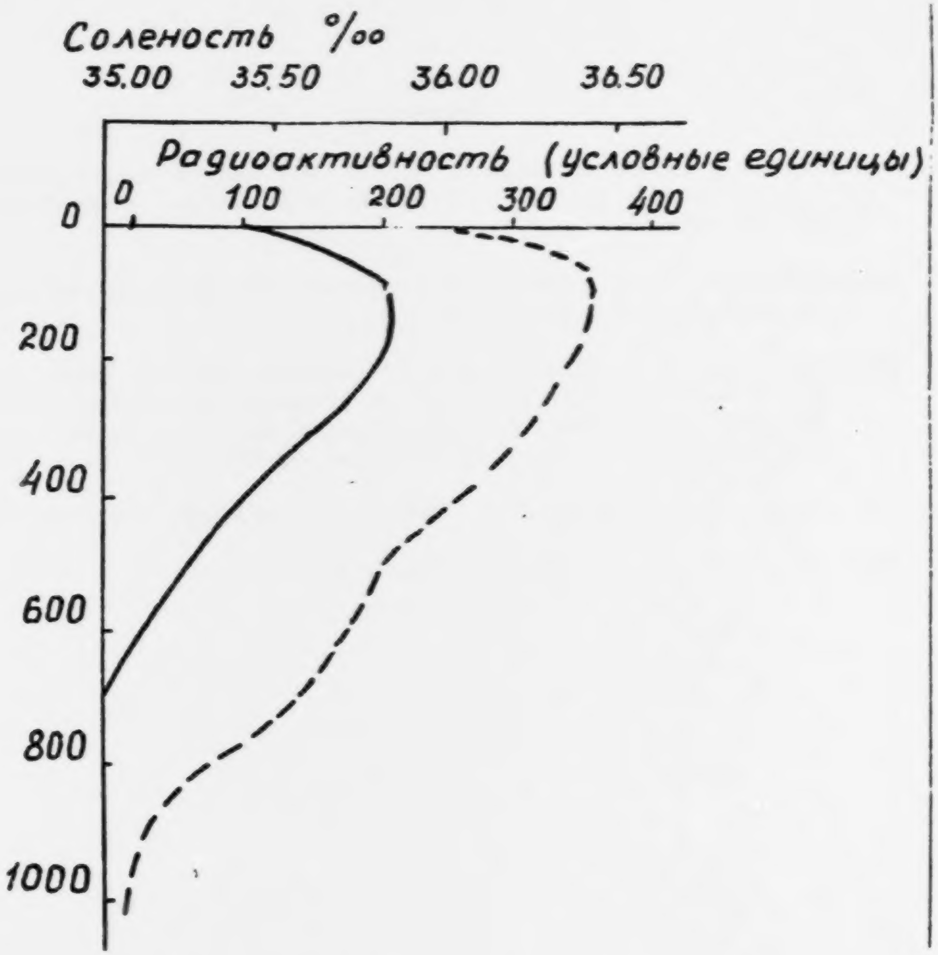


Figure 4. The alteration of the cesium-137 concentration in the Florida Strait (unbroken line), calculated after the salinity (dotted line).

REFERENCES

1. Nelepo, B.A., and M. M. Domanov. 1973. The Ion-exchange Method of the Control of the Cesium-137 Contents in Seawater. Oceanologija,13(4) pp. 602-605.

2. Stepanov, V.N. 1974. The World's Oceans: the Dynamics and Properties of Seawater. M., Znanie, p. 255.

3. Stepanov, V.N., R.P. Bulatov, B.V. Volostnykh, and S.G. Panfilova. 1975. The Formation of the Physical and Chemical Properties and the Water Dynamics of the American Mediterranean Sea. M., Nauka, Trudy, VI Conference on the Sea Chemistry, pp. 79-110.

4. U.S. Atomic Energy Commission. 1968. U.S. AEC Rep. HASL-197. p. 352.

5. Hasl 197, UASEC, N.Y., 10014. 1968. 352 pp.

SUSPENDED PARTICULATE MATTER AND NATURAL RADIONUCLIDES AS TRACERS OF POLLUTANT TRANSPORTS IN CONTINENTAL SHELF WATERS OF THE EASTERN U.S.

Pierre E. Biscaye, Curtis R. Olsen and Guy Mathieu
Lamont-Doherty Geological Observatory of Columbia University
Palisades, New York 10968

ABSTRACT

We have begun to study the dispersion of anthropogenic pollutants by examining the suspended particulate phases with which many pollutants are associated and on which they are transported in the marine environment. The populations of suspended particle types, their distribution, and their associations with trace metal pollutants have been analyzed by examining individual particles, using combined scanning electron microscopy (SEM) and energy-dispersive x-ray fluorescence (EDXRF). The distribution of discrete pollutant particles (e.g. Ti-oxides, and trace-metal bearing organic particles that have their origins in the Apex of the New York Bight) suggests paths by which these pollutants are dispersed across the continental shelf. Gross features of surface and near-bottom suspended particle concentrations reflect vertical and horizontal mixing processes and indicate a flux of particles both into and out of the sediments. The distribution of excess radon, which also diffuses from the sediments (particularly fine-grained sediments), is similar to that of near-bottom suspended particles. The similarity in the horizontal and vertical distribution of this natural tracer to that of suspended particles (particularly during times of vertical stratification of the water column) suggests that the modelling the dispersion of radon will yield information on the rates of dispersion and removal of suspended particulates from the water column.

INTRODUCTION

The role of suspended particles in the marine cycles of many elements only recently received attention from a quantitative point of view. The work of A.P. Lisitzin (7 and references therein) may be regarded as a pioneering effort in the nature and role of suspended particulate matter in the marine environment. The sources of suspended particles to marine waters are multiple and difficult to resolve: continental runoff and fluvial detritus, infall of atmospheric dust, in situ production (primarily in the euphotic zone by biologic activity), and direct anthropogenic inputs (especially adjacent to heavily populated, industrial areas such as New York). For example, Gross (6) estimates that the quantity of waste material dumped in the shelf waters adjacent to the New York metropolitan area exceeds that transported by littoral drift processes and by rivers including the Hudson River which debouches into the New York Bight at New York City. The New York Bight is that area of the continental shelf that lies within the coastline angle made by the intersection at New York City of Long Island (New York) and New Jersey. These wastes include industrial solids and liquids, construction rubble, sewage sludge and harbor dredge spoils (much of which is fine-grained), and carry a significant burden of trace metals and other pollutants.

Once removed from the water column by adsoption onto or incorporation into particulate matter which has settled to the bottom, pollutants and their particulate hosts do not remain forever out of the system. Complex chemical processes (of which most are related to biological processes) occur at or near the sediment-water interface and may alter the chemical and physical state of the pollutants. In addition, particulate-associated pollutants may be reintroduced into the water column and undergo further dispersion by resuspension. In areas of the deep sea where abyssal currents contact the bottom, a significant portion of the suspended particulate standing crop in the water column is due to resuspension (2). In the shallow water regions of continental shelves, resuspension of particles and their burden of pollutants may be expected to be even more important.

This paper is concerned with the distributions of suspended particulate matter particularly in the lower part of the water column in the continental shelf and upper continental slope of the New York Bight. These distributions will be compared with that of excess radon-222, a naturally occurring radioactive gas (half life = 3.85 d) that originates in surficial sediments and therefore constitutes a radioactive tracer of near-bottom processes. We will also describe a technique we have used to characterize the nature of suspended particulate matter and its composition.

SAMPLING AND ANALYTICAL METHODS

Our sampling in the New York Bight was done primarily on three seasonal cruises: October 1974 (V32-01), July 1975 (RC 19-01) and January 1976 (RC 19-05). Samples were taken on serial casts of 30-ℓ Niskin bottles for which the bottom proximity of the lowermost bottle was determined by a pinger. The internal springs of these bottles are Teflon-coated, the air that replaces water upon evacuation of the water sample is filtered to prevent contamination from shipboard air. Water samples are sucked directly through preweighed Nuclepore membrane filters (0.4μm pore size; 47 mm diameter) into evacuated flint-glass bottles for subsequent extraction of radon. Thus suspended particle analyses are done on the same 20ℓ sample as used for radon, except in the case of very turbid near-bottom or nearshore water where a separate, smaller aliquot is filtered for suspended particulates. Subsequent handling of the filters to yield a concentration of total suspended particulate matter is described in Biscaye and Ettreim (1) and Brewer et al. (4). The analytical method for radon (extraction by gas exchange and scintillation counting) is essentially the same method as that described by Broecker (5).

Much of the previous work on the composition of suspended particulate matter has been analytical techniques such as carbon-hydrogen-nitrogen analyses of organic constituents, instrumental neutron activation, x-ray fluorescence or atomic absorption analyses on bulk samples. Such characterizations of the bulk nature of the sample have the advantage of results with good analytical precision. The data can be used to derive statistical correlations between various elements as an insight into their geochemical behavior or can be interpreted with the aid of numerical models. Rather than a bulk analytical method, our approach has been to examine discrete particles, using combined scanning electron microscopy (SEM) and energy-dispersive x-ray fluoresence (EDXRF). An advantage is that one observes the nature of the particulate matter directly and can gain morphological information as well as direct information on associations of different particle types and associations of trace metals with particle types. Disadvantages are that this type of data is difficult to quantify and the analytical work is tedious. We regard this type of analysis as complementary to, rather than an alternative to, bulk analytical methods; a program of bulk sample x-ray fluorescence has begun in our laboratory.

SEM-EDXRF CHARACTERIZATION OF NEW YORK BIGHT SUSPENDED PARTICULATE MATTER

Small portions of Nuclepore filters are mounted on SEM stubs, vapor-coated with carbon and palladium and examined in the SEM. The EDXRF probe attached to our SEM can detect characteristic x-rays from elements with atomic number 9 or greater. Therefore, major constituents of organic matter (such as carbon and nitrogen) are not detected. The classification scheme of major particle types is given in detail in Biscaye and Olsen (3) and consists of two major divisions--Biogenic and Nonbiogenic (each contains two or more subdivisions). Biogenic particles include both those consisting primarily of organic material and those consisting of inorganic test material such as calcium carbonate, strontium sulfate, or opaline silica (such as the diatoms in Fig. 1). The organic particles show either no x-ray spectrum (and therefore consist of elements with atomic number less than nine) or are characterized by the presence of phosphorus with or without accompanying sulfur, chlorine, or both. An example of this kind of organic particle and its x-ray spectrum is shown in Fig. 2.

The other major division, Nonbiogenic, consists primarily of aluminosilicate particles (which includes clay, as well as non-hydrous minerals) characterized by the presence of aluminum and silicon x-ray lines with varying combinations of sodium, magnesium, potassium, calcium, and iron. Other nonbiogenic particles, however, include non-aluminosilicate minerals such as quartz, pyrite, dolomite, barite, sphene and oxides of iron and titanium. Examples of nonbiogenic particles and their characteristic x-ray spectra are given in Figs. 3, 4, and 5. Clues to the identity of a given particle are sometimes conveyed in its morphology as in the obvious case of the diatoms in Fig. 1 or, less obviously, in Figs. 3 and 5. But for the overwhelming majority of particles, many of which are broken and fragmented, identification of the nature of the particle is only possible from the x-ray spectra.

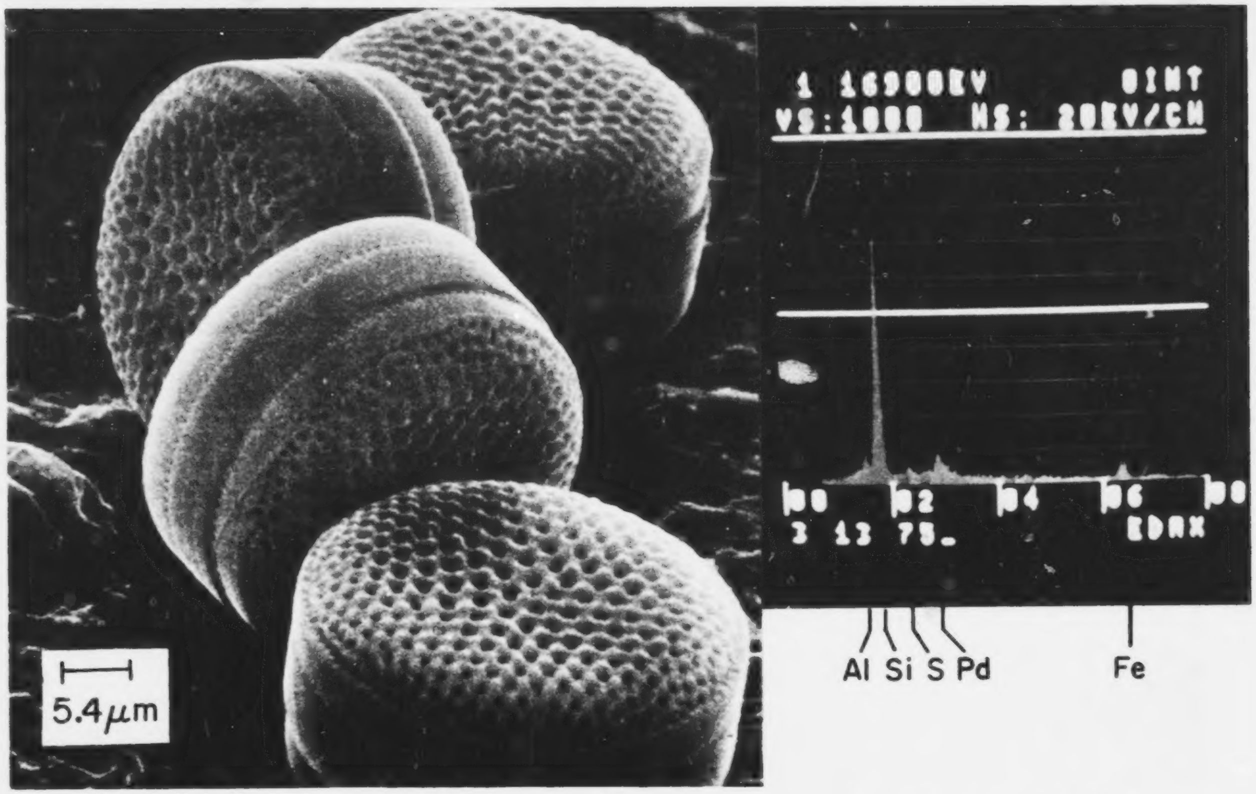


Figure 1. Siliceous centric diatoms from the Bight apex. Note the Fe peak in the x-ray spectrum. Fe and frequently Ti coat much of the suspended matter in the apex. Palladium on this and all the x-ray spectra shown (Figs. 2 to 5) is from the metallic vapor coating used to prepare the sample for SEM.

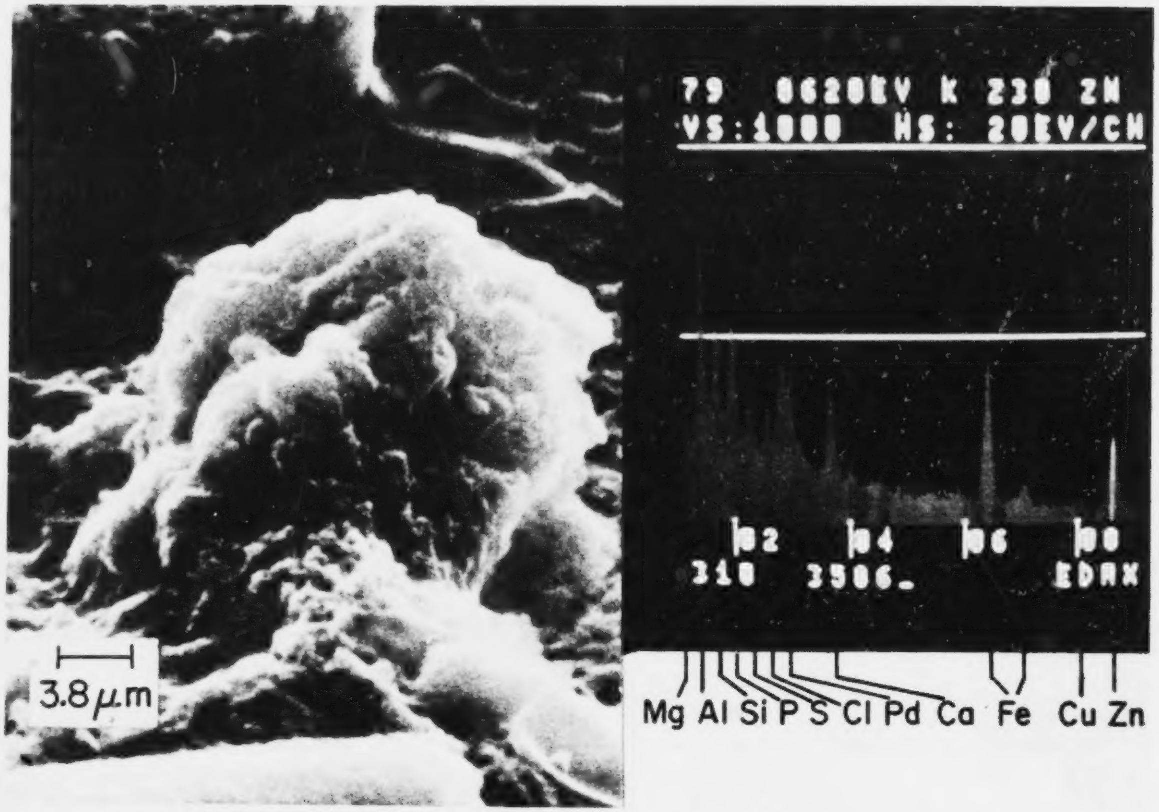


Figure 2. Organic particles from the waters of the Bight apex, near the disposal sites for sewage sludge and dredge spoils. Note definitive P peak and high concentrations of Fe, Cu, and Zn.

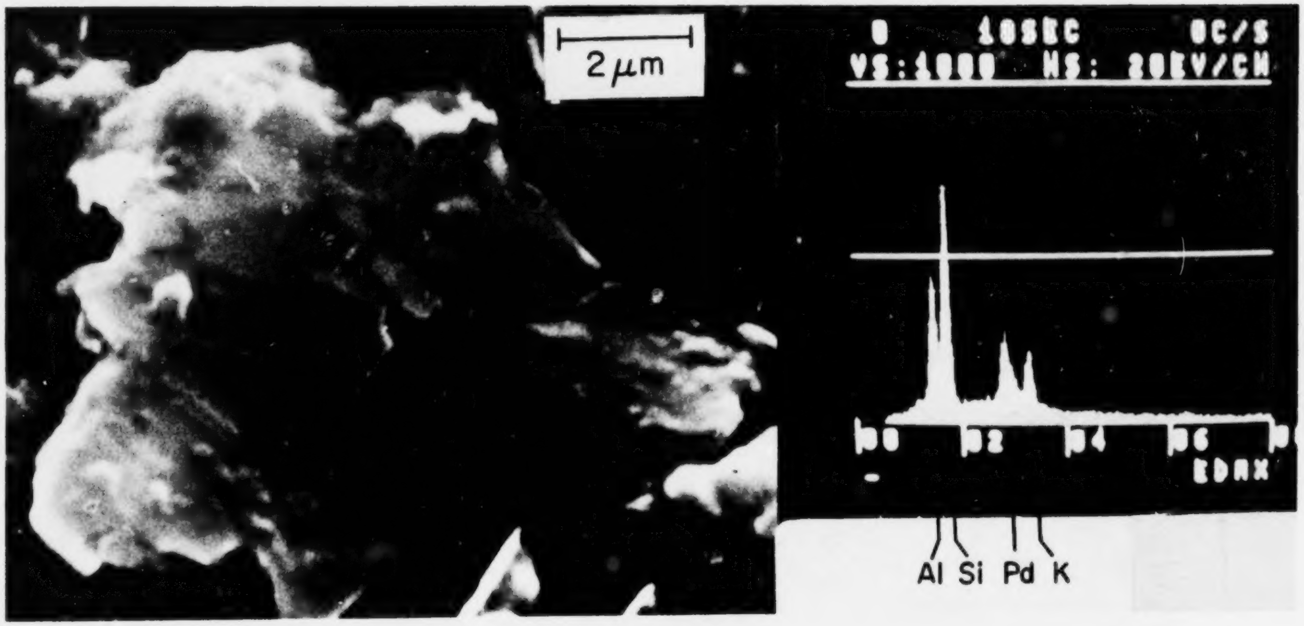


Figure 3. Muscovite flake from near-bottom waters of the outer shelf.

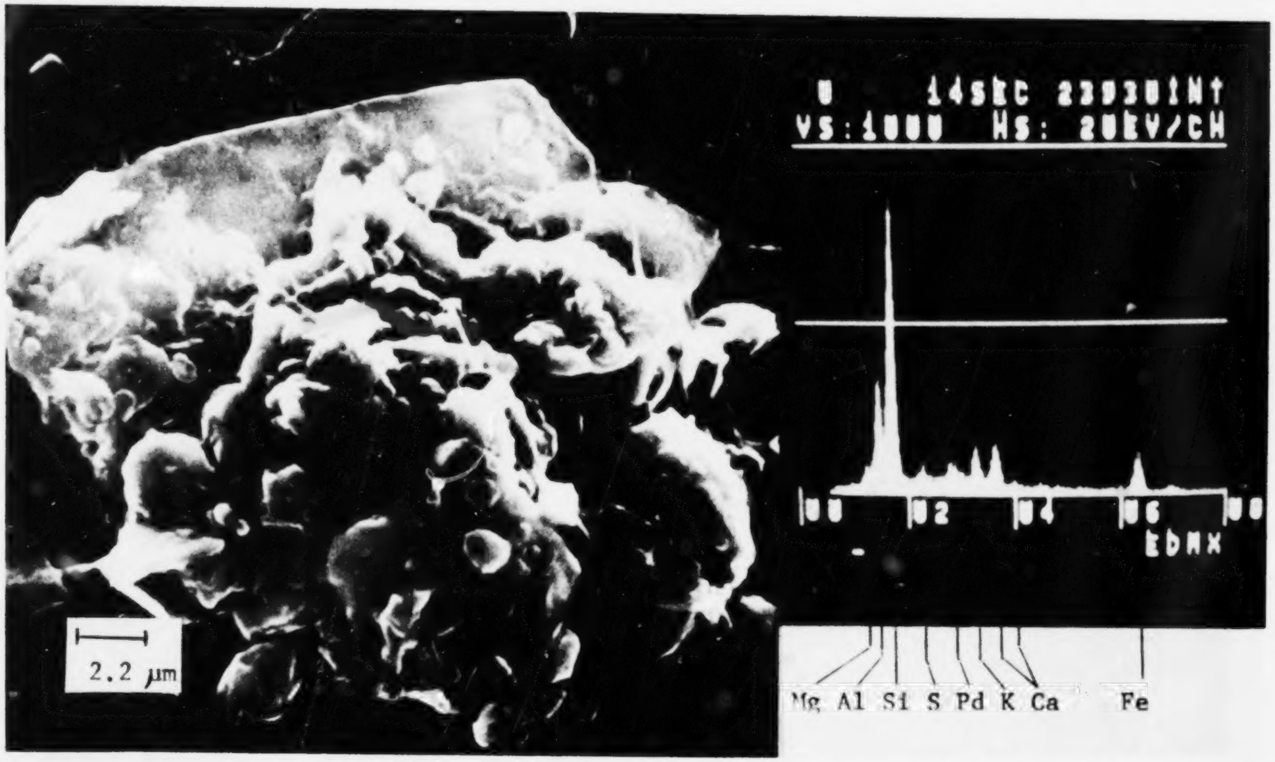


Figure 4. Aggregate of Mg-K-Ca-Fe aluminosilicate suspended particle typical of near-bottom waters of the outer continental shelf and upper continental slope.

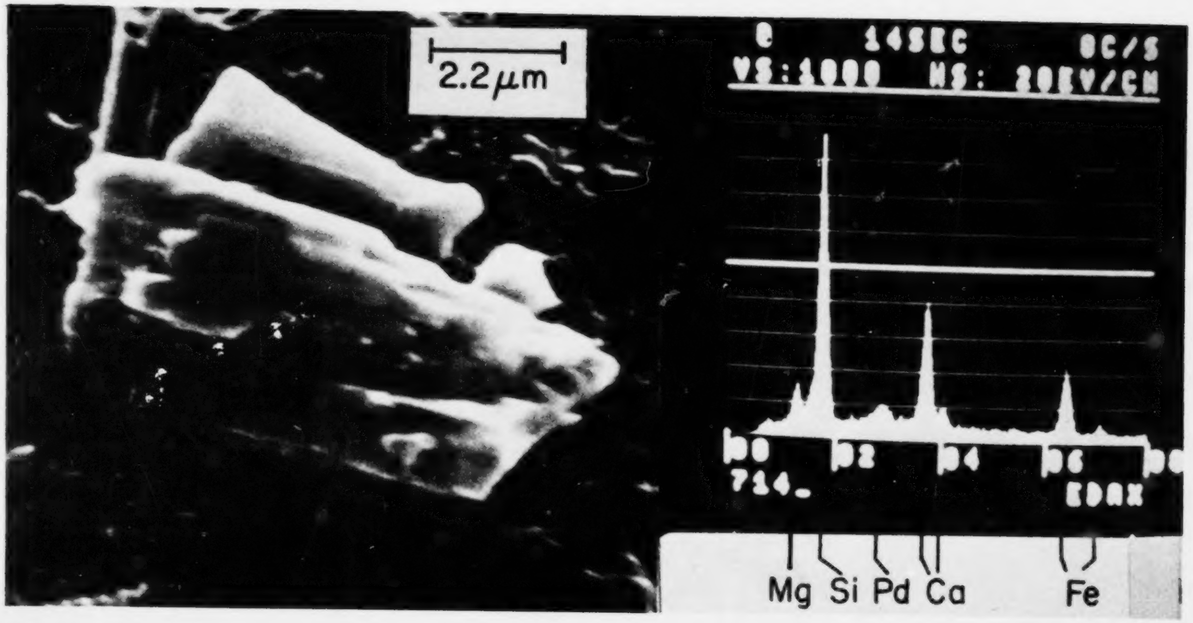


Figure 5. Pyroxene grain from near-bottom waters of the upper continental slope. Note cleavage which sometimes aids in identification of specific minerals, e.g. pyroxenes, micas, feldspars, dolomite, etc.

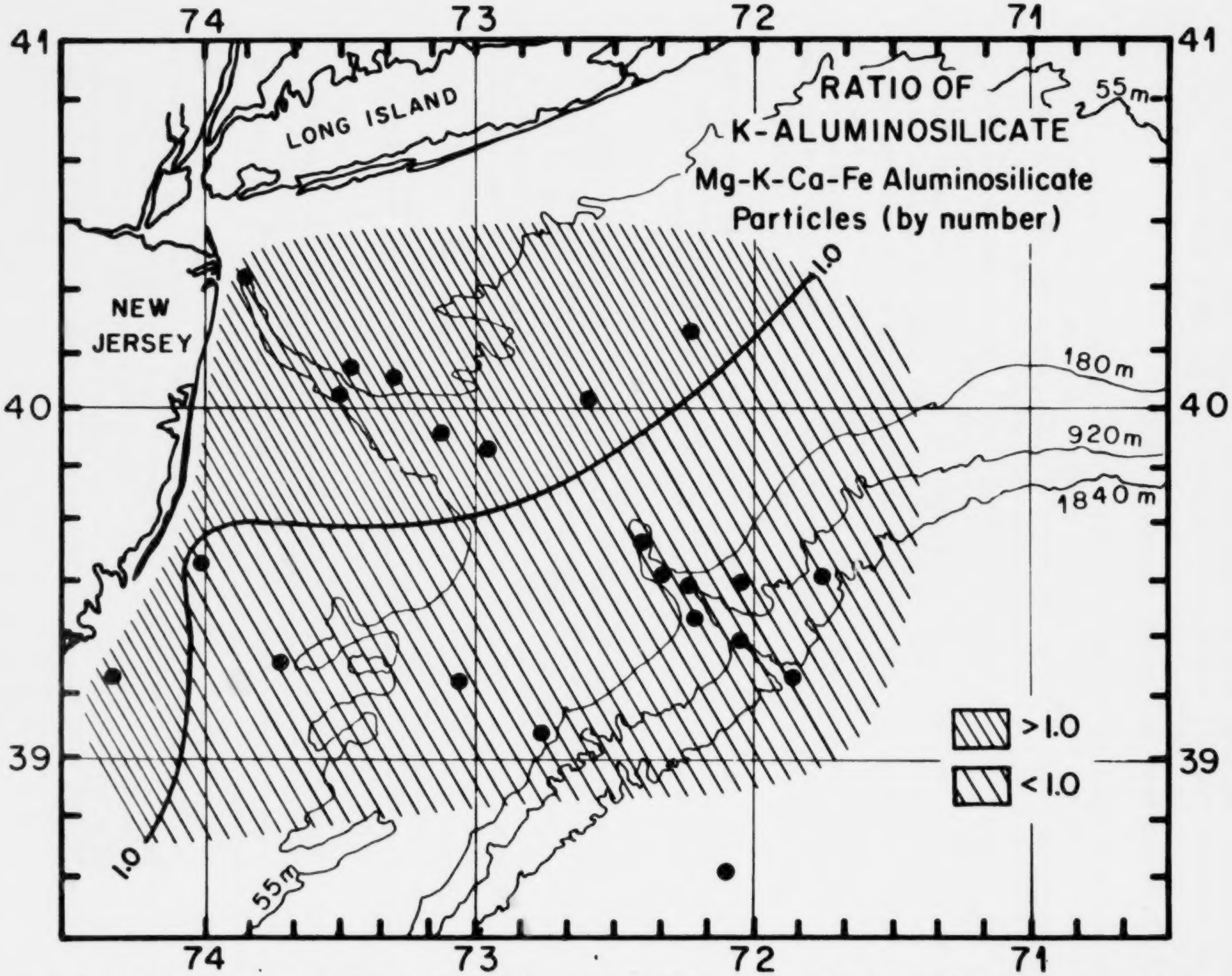


Figure 6. Ratio of the abundance (by number of particles) of K-aluminosilicates to Mg-K-Ca-Fe aluminosilicates in near-bottom waters of the New York Bight. Note the sharpe decrease in the ratio toward the edge of the continental shelf and beyond.

We have thus far examined primarily filters taken within about 10 meters of the bottom and can make the following generalizations about the distribution of particle types in the New York Bight.

The biogenic skeletal debris is predominantly siliceous, consisting primarily of diatoms (Fig. 1) with some silicoflagellates and a few radiolarian fragments. Calcareous skeletal debris (primarily coccoliths) becomes more abundant in waters near and beyond the shelf break.

Organic particles in nearshore waters are characterized by strong P peaks relative to Si and Al, indicating little aggregation with or incorporation of aluminosilicate material. These nearshore organic particles are frequently observed to contain high concentrations of Fe, Mn, Ti, Cu, Sn, Cr, Zn, Pb, Ni, and/or As. Although organic particles containing Fe and Mn are ubiquitous in the New York Bight, those detectable (at least per mil) quantities of Ti, Cu, Sn, Cr, Zn, Pb, Ni, and As, are most abundant in the Bight Apex (near the outflow of the Hudson River) and the disposal sites for sewage sludge and dredged harbor spoils. Consequently, it appears that the dumped wastes are the most likely source for these rare metal-bearing organic particles. Their dispersal from the Bight Apex may be useful in studying particle transport processes on the shelf. In addition, detectable concentrations of trace metals (other than Fe and Mn), when observed, were almost invariably associated with organic particles.

Organic particles in the outer shelf waters (especially near the bottom) were commonly observed as large masses of organic-clay aggregates, showing a relatively small P peak but only occasionally detectable trace metals (other than Fe and Mn).

Although organic matter and skeletal debris comprise a considerable portion of the suspended matter in the surface and intermediate waters of the Bight, there is a marked decrease relative to the nonbiogenic fraction in near-bottom waters. The nonbiogenic fraction consisted of clay aggregates and individual mineral grains. The bulk clay mineral composition of the suspended matter in the Bight is more than 50 per cent illite with less chlorite, and still less montmorillonite, mixed layer clays, and kaolinite (8). Identifiable mineral grains consisted of quartz, K-feldspar, palgioclase, muscovite (Fig. 3), biotite, chlorite, dolomite, and heavy minerals such as amphiboles, pyroxenes (Fig. 5), sphene and barite.

A marked change in mineralogy of the aluminosilicate suspended matter occurs at the shelf break. In nearshore waters, and in surface waters of the outer shelf, the predominant aluminosilicates are K-rich. In the near-bottom waters along the upper continental slope and in the Hudson Canyon, Mg-Ca-K-Fe other seasons, the concentrations are high in the Hudson Canyon and low in the zone parallel to the slope and centered at ∿ 1500-2000 m depth. Strong verticle and horizontal mixing over most of the shelf during January blurs the differences between surface-produced and resuspended particle distributions. This contrast with the July data points up the importance of the thermocline in separating the two regimes and the processes that control the distribution of particulate matter within them.

The distribution of near-bottom excess radon for the three cruises is shown in Figs. 12, 13, and 14. Several features of these distributions, similar to those of the distributions of near-bottom suspended particles (Figs. 7, 8, and 9), point to their similar origins and suggest that their distribution in the water column is controlled by similar processes. These features are: (1) patches of high concentrations of excess radon approximately coincident with those of suspended particulate matter (as in the suspended particles, the patches of high concentrations of radon are less distinct during the stratified October and July regimes); (2) coincidence of the upper slope zone of minimum concentration of suspended particles (centered somewhere between about the 1500 and 2000 isobath) with a minimum in near-bottom concentration of excess radon.

Comparison of both the near-bottom suspended particulate and excess radon distributions with the distribution of bottom sediment type suggests in part, the control for the observations. The parameter chosen to characterize the bottom sediment is the weight percentage finer than 63 μm diameter (Fig. 15). The data are based on samples taken at each location shown in Figs. 7 to 9, but most of the data come from Schlee (10 and unpublished data). The relicit glacial-age Shelf Channel of the Hudson River (approximately defined by the 55m isobath) is seen to be filled with fine-grained sediment and represents a long strip of dark, organic-rich mud in a shelf otherwise largely covered by very clean sands. At the eastern part of the study area lies a much larger area of fine-grained sediments but which, unlike the Hudson Shelf Channel, shows little or no bathymetric control of the fine-grained sediments. Compared with Figs. 7, 8, and 12 to 14, these two patches of fine-grained sediments are seen to be the sources of both the suspended particles and the excess radon in the lower portion of the water column. Vertical profiles of both constituents show that, when thermal stratification of the water column exists, vertical mixing of these bottom-source tracers is limited by the thermocline. But under conditions of lower stability (as obtained during the January 1976 cruise), both resuspended particles and excess radon are mixed upward to the surface. The displacement of the plumes of these tracers from their fine-grained sediment sources is a measure of the advective and diffusive forces of dispersion acting in the water column on the shelf. Modelling of these data in an attempt to quantify these dispersive forces is in progress and will be the subject of another paper.

The problem of the zone of minimum near-bottom excess radon and suspended particles is not answered from the sediment data (Fig. 15); if anything, it is compounded. More than 100 samples of the sediment with a range of grain size characteristics have been measured for their potential to produce excess radon and these data show a correlation between radon productivity and the weight percentage of the sample finer than 63 μm. The fine-grained sediments of the aluminosilicates overwhelmingly dominate. This difference is shown in Fig. 6.

Discrete Ti (oxide) particles (a few microns in diameter) have been observed at several depths in the Bight Apex near the disposal sites for sewage sludge and acid Fe-Ti wastes. In addition, Fe and Ti coatings can be seen on much of the suspended matter, including plankton (Fig. 1) in this area of the Bight. Both the abundance of Fe- and Ti-coated and Ti (oxide) particles decrease away from the Bight Apex, indicating their potential as tracers for particle dispersal.

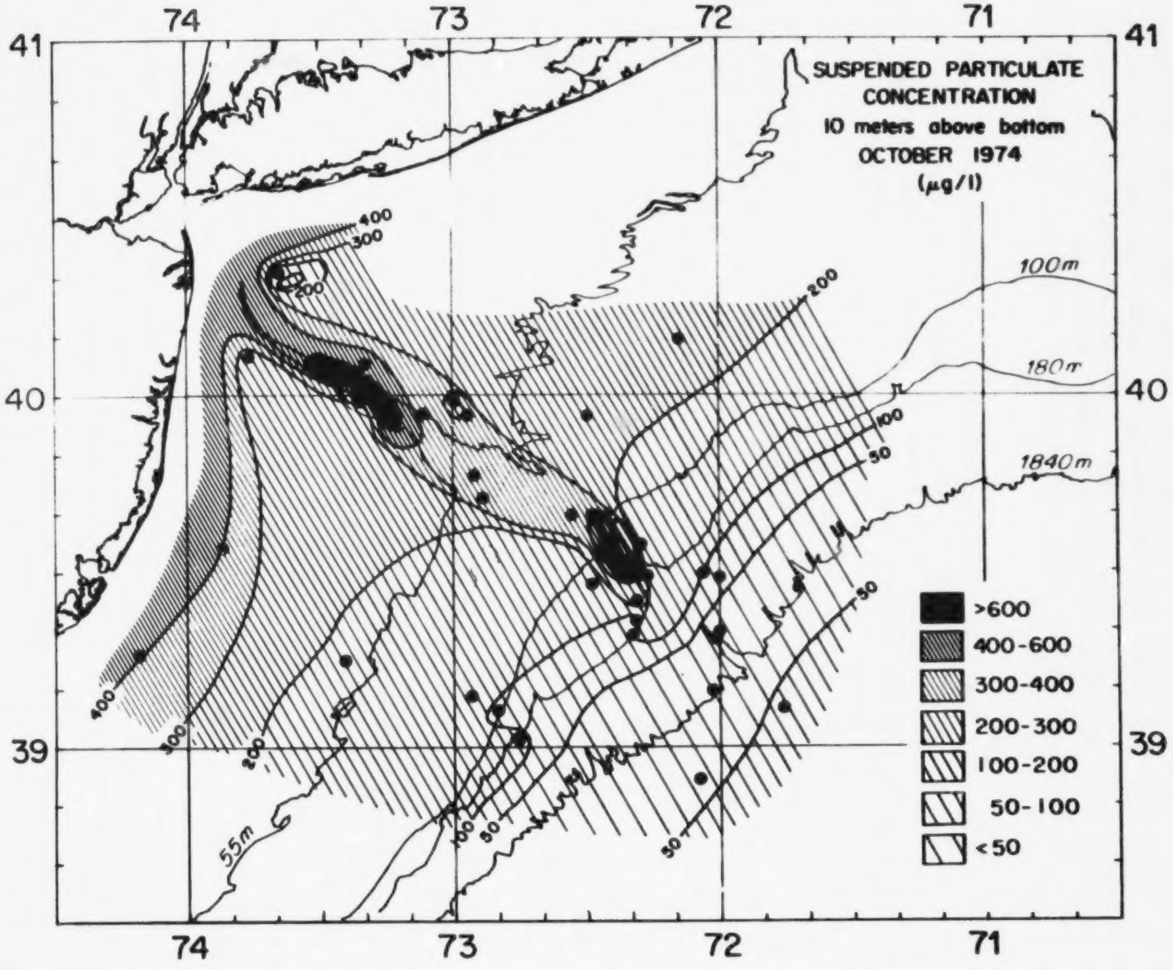


Figure 7. Concentration of suspended particles (μg/ℓ) 10 meters above bottom (mab) during October 1974.

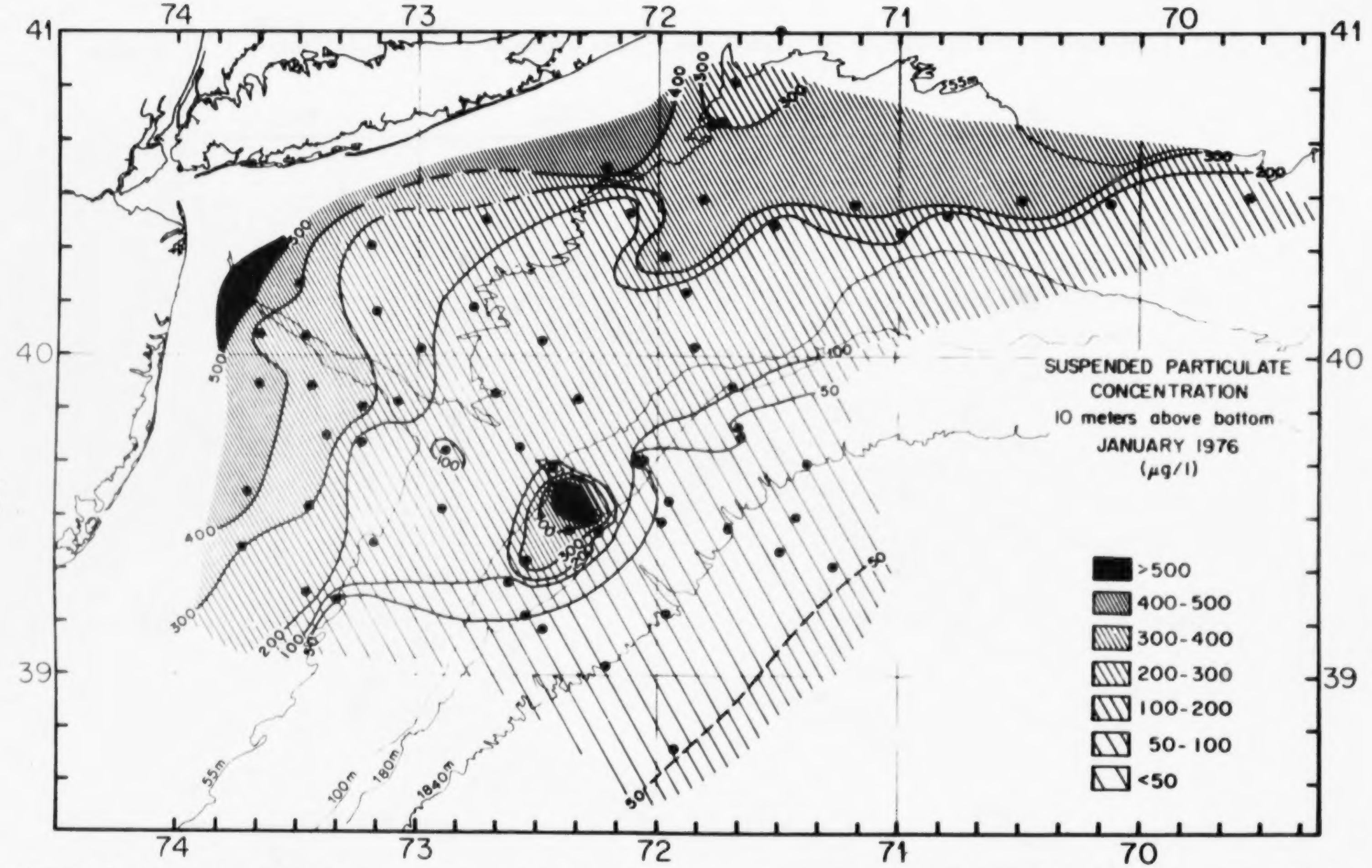


Figure 8. Concentration of suspended particles (μg/ℓ) 10 meters above bottom (mab) during January 1976. Note that the patch of high concentrations associated with the Hudson Shelf Channel in October and July does not exist in January, but that the deeper water anomaly in the Upper Hudson Canyon remains.

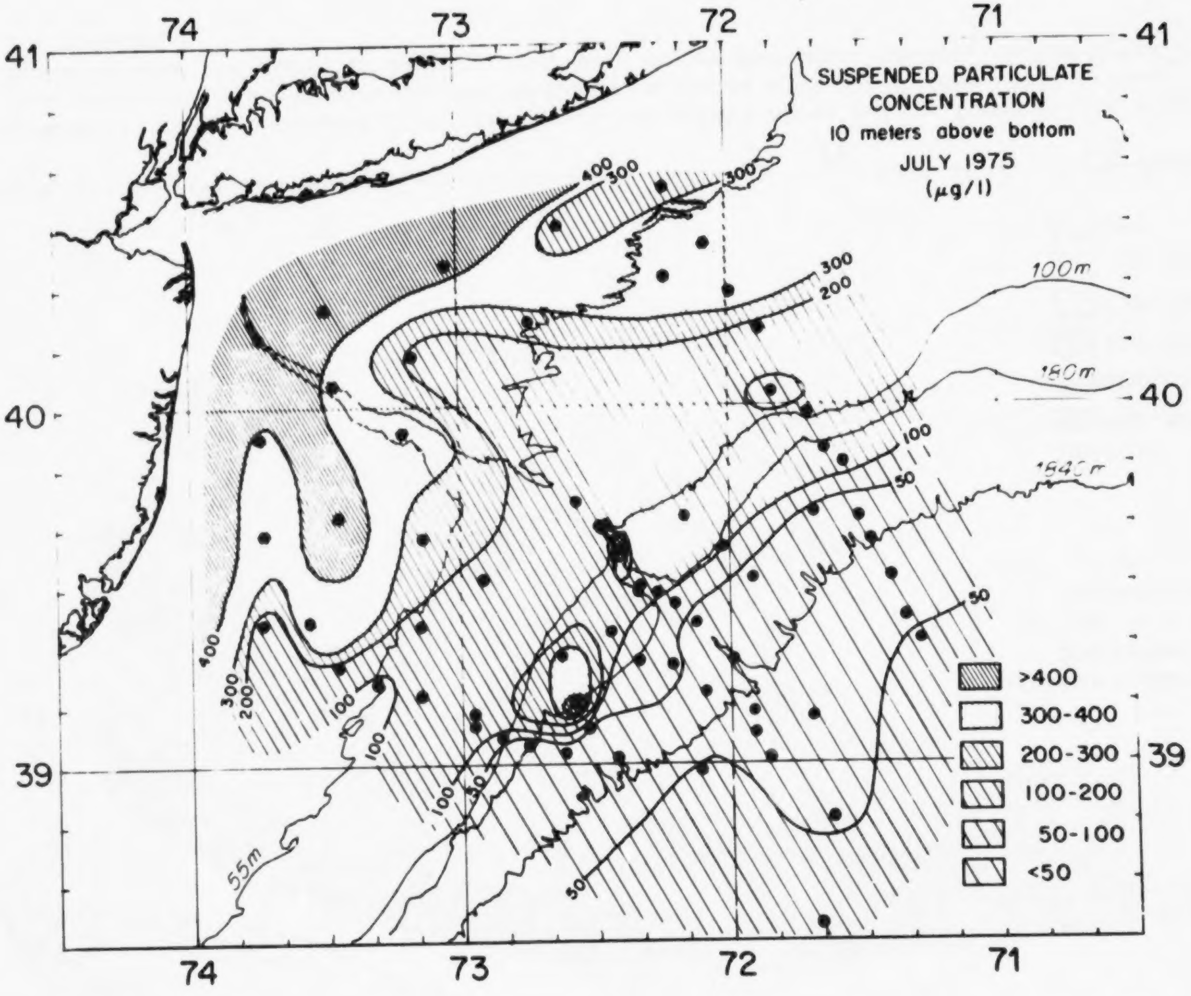


Figure 9. Concentration of suspended particles (μg/ℓ) 10 meters above bottom (mab) during July 1975.

Reproduced from best available copy.

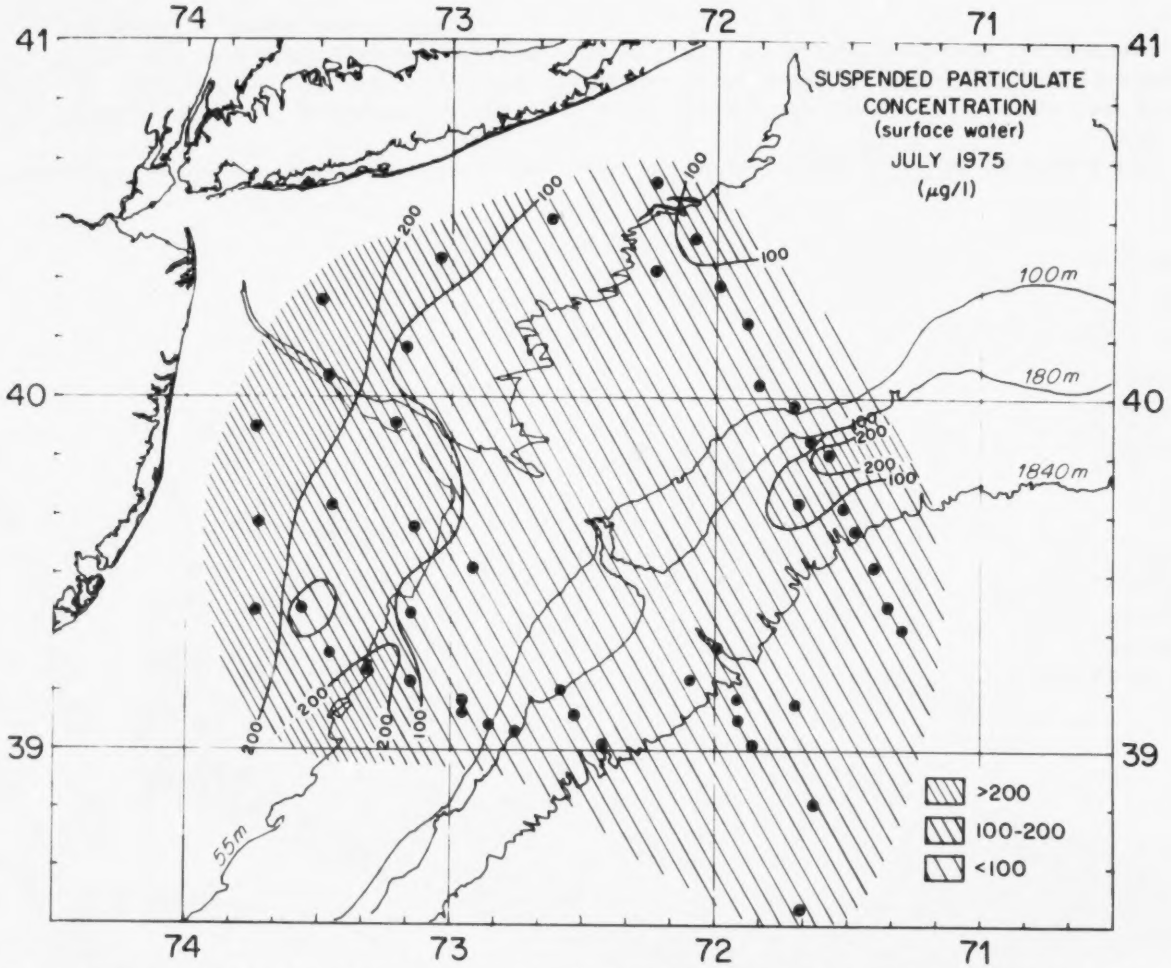


Figure 10. Concentration of suspended particles (µg/ℓ) in surface water during July 1975. Note that both the 200 and 100 µg/ℓ isopleths are nearer the coastline than at 10 mab (Fig. 8). Note also that local high concentration anomalies at 10 mab such as those adjacent to the Hudson Shelf Channel and in the Hudson Canyon do not extend to the surface.

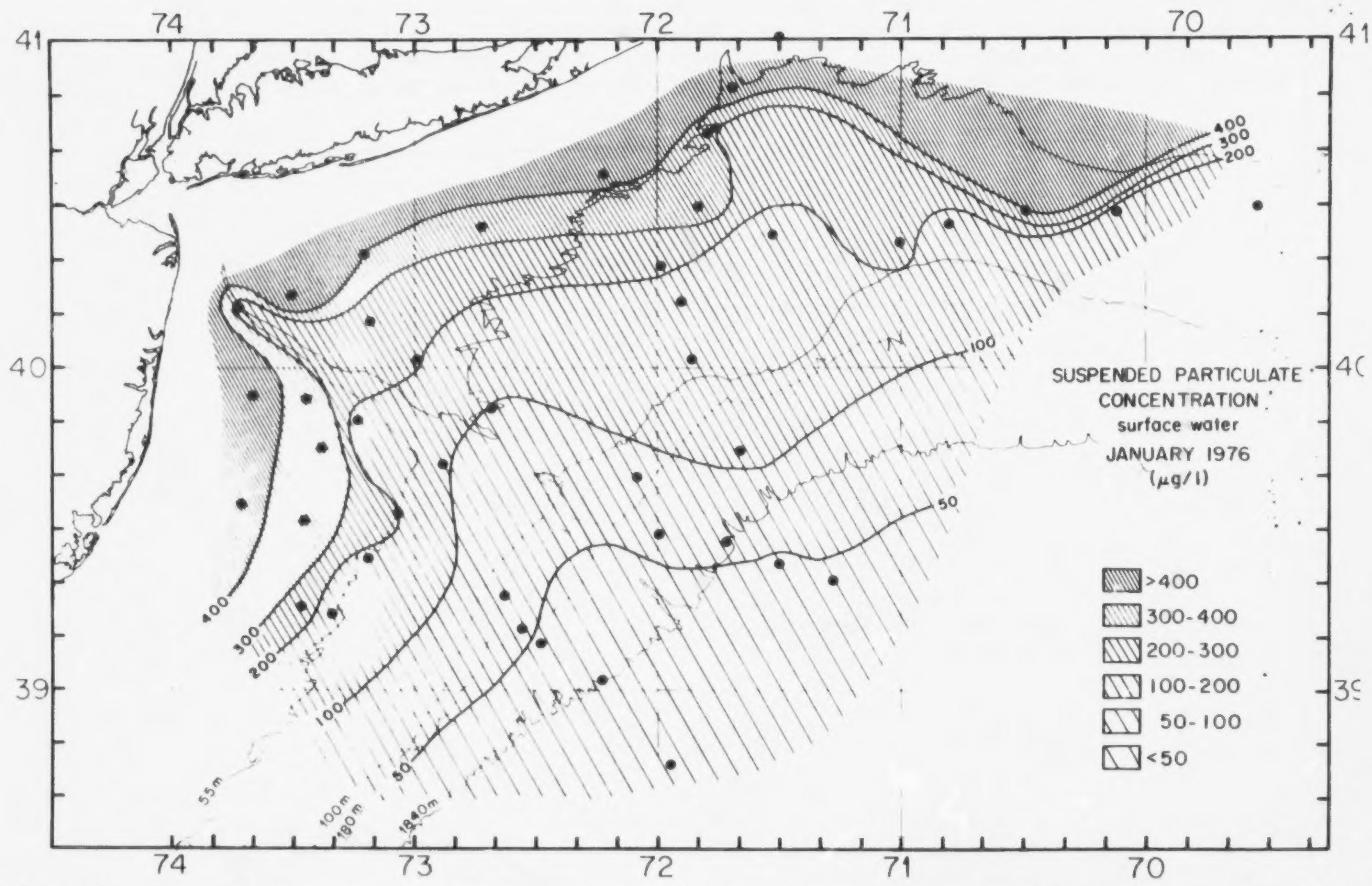


Figure 11. Concentration of suspended particles (μg/ℓ) in surface water during January 1976. Note that the position of the isopleths are essentially the same as those for particulates 10 mab (Fig. 9), suggesting that vigorous vertical mixing has homogenized the particulate populatio through the shelf water column.

DISTRIBUTIONS OF SUSPENDED PARTICULATE MATTER AND EXCESS RADON

The distributions of suspended particulate matter and excess radon discussed in this section must be viewed with the following limitations in mind. First, the sampling on each cruise took place over a period of two weeks and therefore, although assembled in a single figure, the data are not strictly synoptic. We are aware of temporal variability in both particulate and excess radon concentrations on the order of days or even hours. The similarity of the gross features for data sets from three different seasons, however, supports the validity of these general conclusions. Second, because our paper focuses on near-bottom processes, the bottom, rather than the sea surface, is taken as the reference level. This becomes a graphic convenience because of the great depth range (10-3000 m) over which sampling was done on each cruise.

The distributions of total suspended particulate concentrations at 10 meters above bottom are shown in Figs. 7, 8, and 9 for the October 1974, July 1975, and January 1976 cruises, respectively. The principal features are: (1) a seaward decrease across the shelf in the concentration of particulate matter; (2) localized patches of high concentrations of suspended particles superposed on this general decrease most strikingly over the Hudson Shelf Channel and Hudson Canyon. (The near-bottom localization of high concentrations associated with the Hudson Shelf Channel [defined by the 55 m isobath] in October [Fig. 7] and displaced southwest from it in July [Fig. 8] is not evident in the January data set [Fig. 9]); (3) a zone beyond the shelf break (>100 m water depth) approximately parallel to the isobaths near the bottom that extends over about a kilometer of water depth in which the concentration (or standing crop) of suspended particles goes through a minimum and, from a limited number of data points, appears to rise again in deeper water. The center of this zone is somewhere between the 1500 and 2000 m isobath.

These distributions of particle concentrations 10 meters above the bottom may be compared to particle concentrations in surface water in July 1975 and January 1976 (Figs. 10 and 11, respectively; surface samples were not taken on the October cruise). During July, although the surface water concentrations decrease seaward, they do so more rapidly with distance from shore than do particulate concentrations near the bottom. At that time, some degree of patchiness is seen in the surface-water concentrations but the locations of patches of high concentrations bear no geographic relation to those seen near the bottom. After comparing the January surface (Fig. 11) and near-bottom data (Fig. 9), there is little difference in the distribution of concentrations until beyond the shelf break. Beyond ∿ 100-200 m water depth, as in the upper continental slope have the greatest potential to produce excess radon of any sediments in the study area rendering the near-bottom low-radon zone over the slope at 1500 to 2000 m even more anomalous. Bottom photographs and visual observations (Bruce Heezen of Lamont-Doherty Geological Observatory and Wilford Gardner of Woods Hole Oceanographic Institution, personal communication) of this area show very clear water conditions underlain by very fine-grained, almost soupy sediments. By direct observation, these sediments can be easily resuspended if distributed by any mechanism.

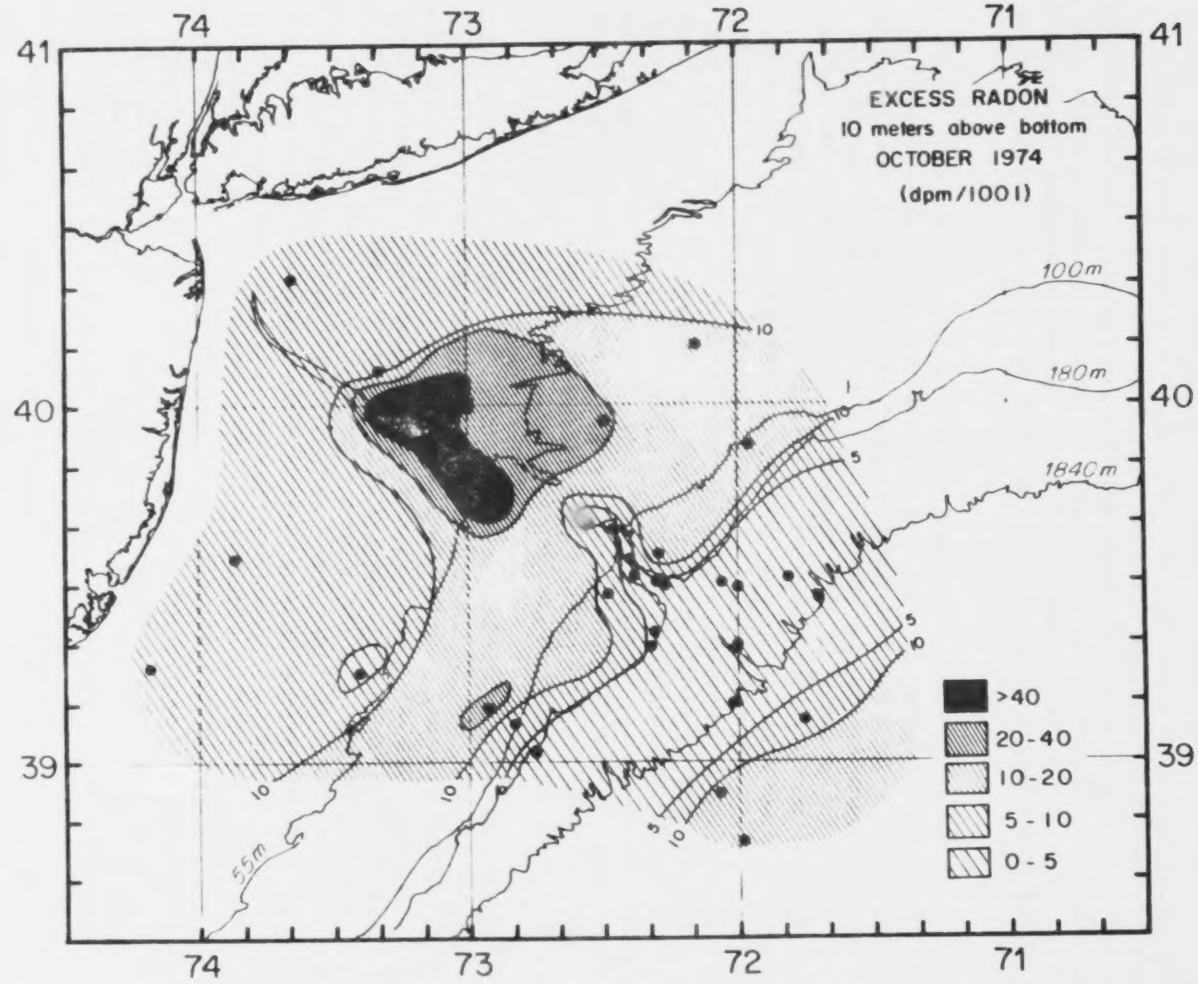


Figure 12. Concentration of excess radon (disintegrations per minute, dpm/100 ℓ) in water 10 mab during October 1974. Note the coincidence of high concentrations of radon and suspended particles on the shelf and low concentrations in the deep water zone along the upper continental slope (Fig. 7).

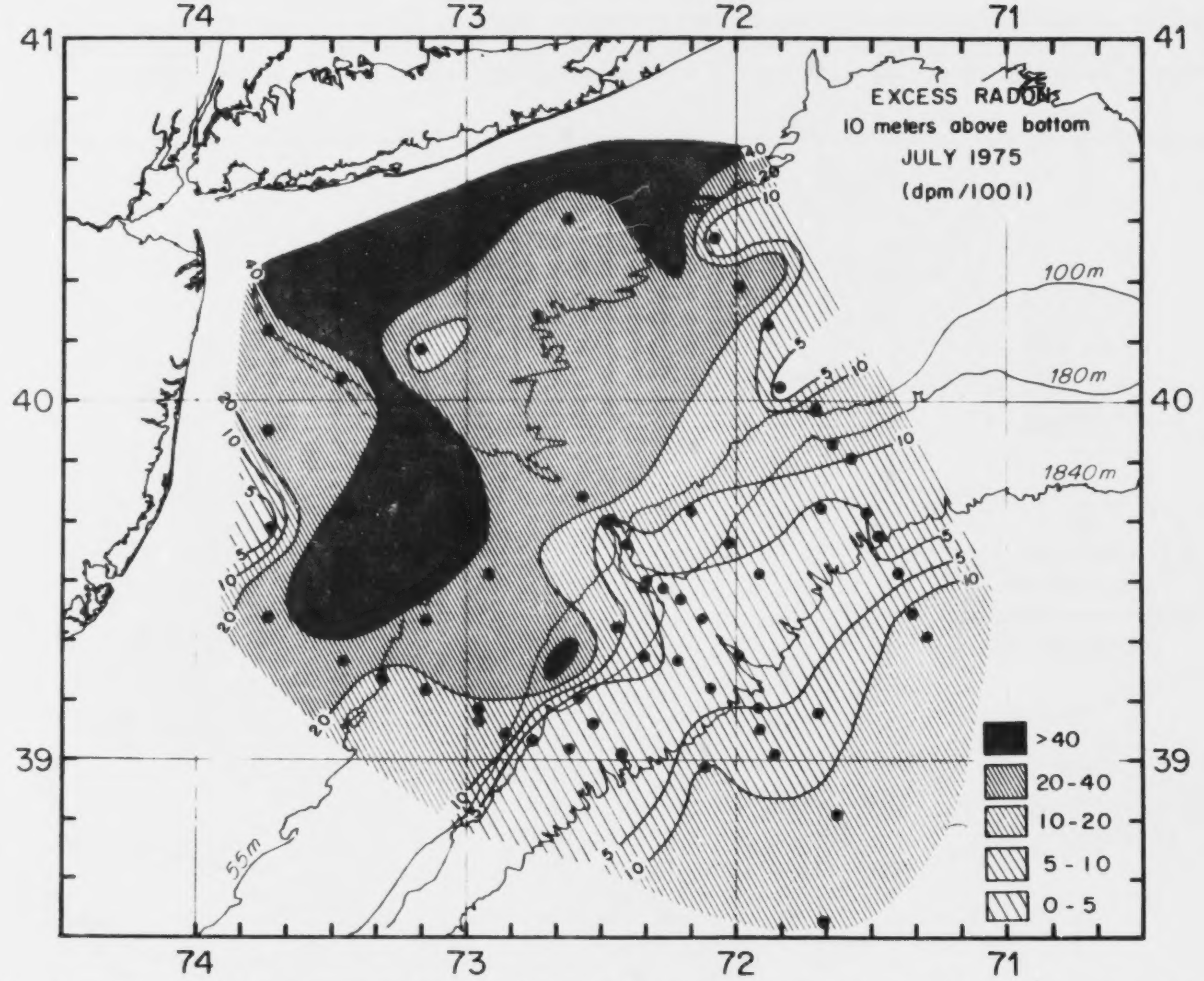


Figure 13. Concentration of excess radon (disintegrations per minute, dpm/100ℓ) in water 10 mab during July 1975. Note the coincidence of high concentrations of radon and suspended particles on the shelf and low concentrations in the deep water zone along the upper continental slope (Fig. 8).

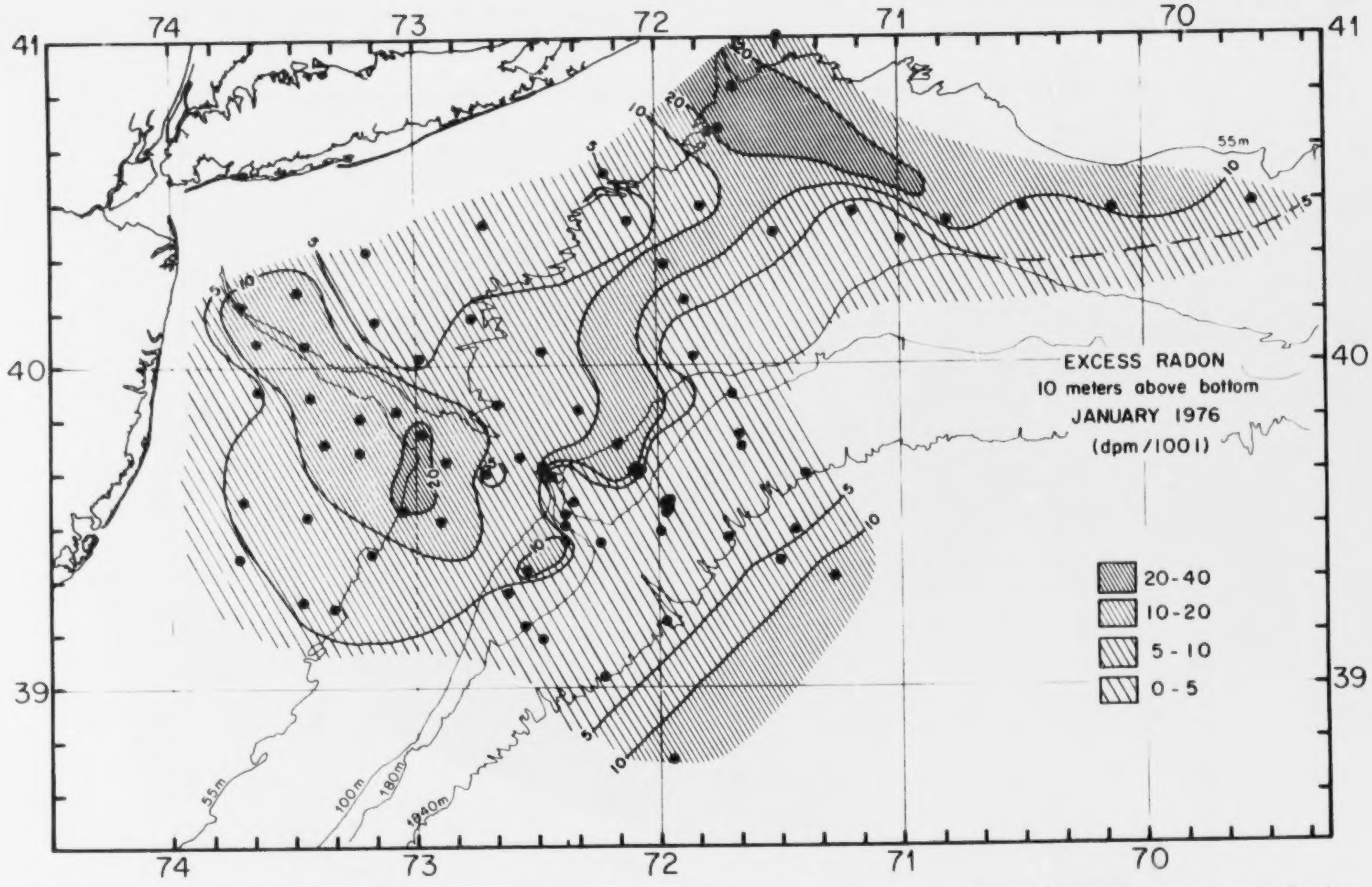


Figure 14. Concentration of excess radon (disintegrations per minute, dpm/100ℓ) in water 10 mab during January 1976. Note that, although the zone of high concentration water associated with the Hudson Shelf Channel is still visible in the January data, the concentrations of excess radon are lower than in July (Fig. 13) or in October (Fig. 12).

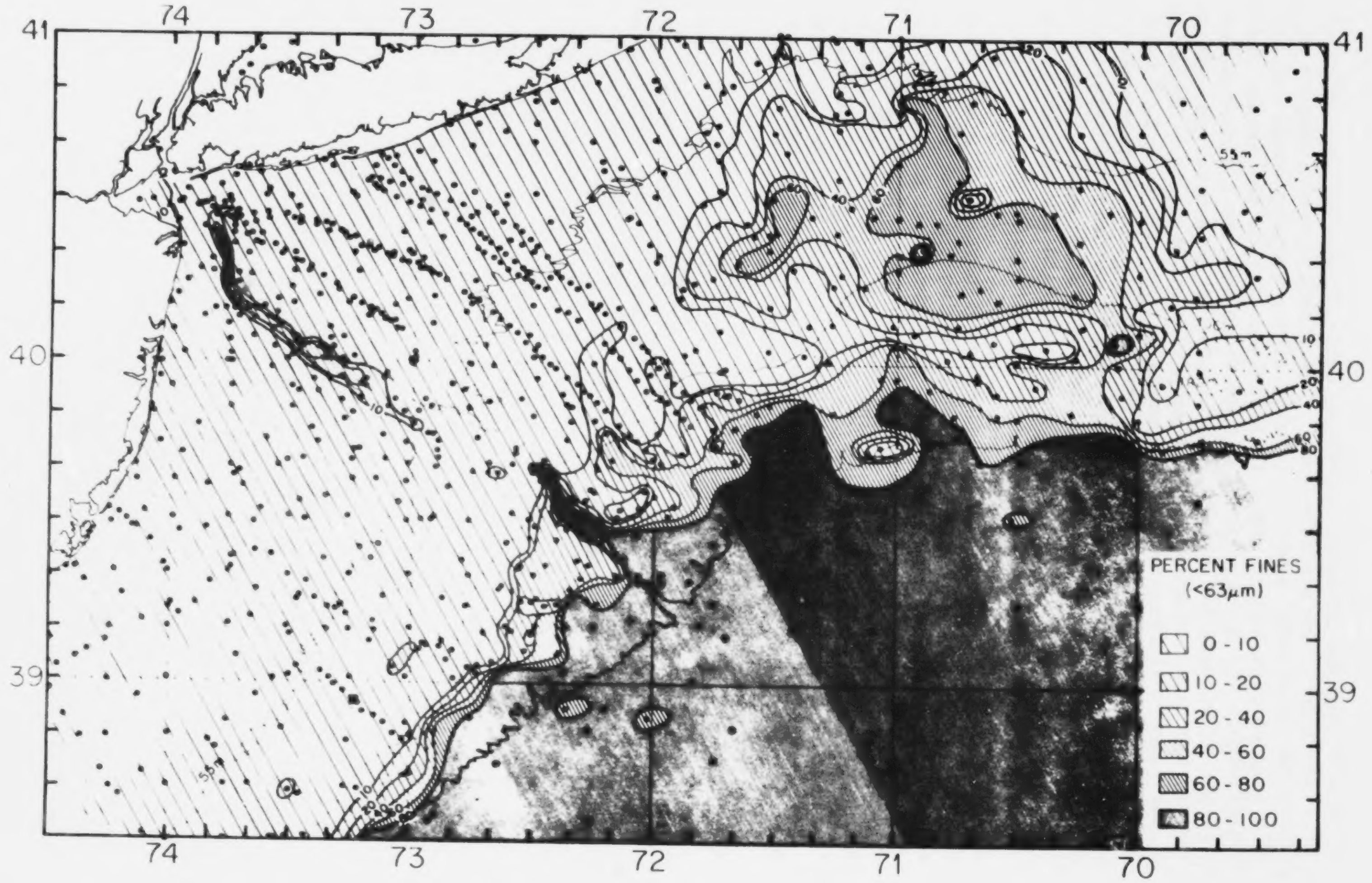


Figure 15. Distribution of percent fines (weight % < 63μm) in surface sediments.

Reproduced from
best available copy.

At present we see two possible, opposing explanations for our observations in this low-radon, low-particle zone. The first is that, despite many casts in which our lower-most sample was taken within several meters of the bottom, this zone of near-bottom water is so quiescent that the excess radon being produced within the sediments and diffused across the sediment-water interface is not mixed vertically more than a meter or so and we have missed sampling the excess radon standing crop on several tens of casts. Comparing this to excess radon measurements made elsewhere in the deep sea (1, 9, and references therein) would indicate an area of extremely low vertical mixing. Elsewhere, excess radon is observed to extend tens to hundreds of meters above the bottom. The reason that this extreme quiescence, if true, is limited to this depth range is not known. It does not coincide with any obvious hydrographic parameters.

The second explanation is that some mechanism of horizontal mixing, acting over one-half to one-kilometer depth, is exchanging the near-bottom (excess radon-rich) water with mid-depth water from the oceanic interior that would also be low in suspended particles (compared to water further up the slope) and would contain no excess radon. Such mixing must be sufficiently rapid to dilute the flux of excess radon from the sediments to undetectable levels very near the bottom, but of a nature that does not stir up the bottom sediments. We hope to be able to distinguish between these explanations as the result of measurements to be made on future cruises.

Acknowledgments

We thank H. James Simpson and Taro Takahashi for reviewing this paper. Financial support for this work was provided by the U.S. Energy Research and Development Administration under Contract EY-76-S-02-2185. Lamont-Doherty Geological Observatory Contribution No. 2501.

REFERENCES

1. Biscaye, P.E., and S.L. Eittreim. 1974. Variations in Benthic Boundary Layer Phenomena; Nepheloid Layers in the North American Basin. In: Suspended Solids in Water, R. Gibbs, ed. p. 227-260.

2. Biscaye, P.E., and S.L. Eittreim. 1974. Suspended Particulate Loads and Transports in the Nepheloid Layer of the Abyssal Atlantic Ocean. Marine Geology, v. 23, p. 155-172.

3. Biscaye, P.E., and C.R. Olsen. 1977. Suspended Particulate Concentrations and Compositions in the New York Bight. In: Middle Atlantic Continental Shelf and the New York Bight, M.G. Gross, ed. ASLO Special Symposia No. 2, p. 124-137.

4. Brewer, P.G., D.W. Spencer, P.E. Biscaye, H. Hanley, P.L. Sachs, C.L. Smith, S. Kadar, and J. Fredericks. 1976. The Distribution of Particulate Matter in the Atlantic Ocean. Earth and Planetary Science Letters, v. 32, p. 393-402.

5. Broecker, W.S. 1965. An Application of Natural Radon to Problems in Ocean Circulation. In: Symposium on Diffusion in Oceans and Fresh Waters, T. Ichiye, ed. p. 116-145.

6. Gross, M.G. 1972. Geologic Aspects of Waste Solids and Marine Waste Deposits, New York Metropolitan Region. Geol. Soc. Amer. Bull., v.83, p. 3163-3176.

7. Lisitsin, A.P. 1972. Sedimentation in the World Ocean. S.E.P.M. Special Publ. No. 17, Tulsa, Oklahoma, 218 p.

8. Meade, R.H., P.L. Sachs, F.T. Manheim, J.C. Hathaway, and D.W. Spencer. 1975. Sources of Suspended Matter of the Middle Atlantic Bight. J. Sediment. Petrol. v. 45, p. 171-188.

9. Sarmiento, J.L., H.W. Feely, W.S. Moore, A.E. Bainbridge, and W.S. Broecker. 1976. The Relationship between Vertical Eddy Diffusion and Buoyancy Gradient in the Deep Sea. Earth and Planetary Science Letters, v. 32, p. 357-370.

10. Schlee, J. 1975. Sand and Gravel. MESA New York Bight Atlas Monograph 21, New York Sea Grant Institute, Albany. 26 pp.

TRACE ELEMENT GEOCHEMISTRY OF CONTINENTAL SHELF WATERS OF THE SOUTHEASTERN UNITED STATES*

Herbert L. Windom
Skidaway Institute of Oceanography
P. O. Box 13687
Savannah, Georgia 31406

INTRODUCTION

The greatest exploitation of the marine environment by man has occurred on continental shelves. In the future, the search for mineral resources and sites for nuclear power plants will focus greater activity in this region. If the continental shelves are to be utilized in a logical way, with minimal environmental impacts, it is important to understand processes that are active there.

Most of the activities related to energy development (e.g., petroleum exploration and production, offshore nuclear power plant siting) may result in releases of stable and radioisotopes of naturally occurring trace elements. To predict the fate of these additions and their ultimate impact on the environment, we must develop a fundamental understanding of the natural processes that govern their behavior. This paper discusses aspects of the geochemistry of trace elements that influence their concentration and distribution in continental shelf waters. The trace elements considered are arsenic, copper, mercury, nickel, and zinc. The discussion is based on studies of the continental shelf of the southeastern U.S. coast, referred to as the South Atlantic Bight (Figure 1).

The South Atlantic Bight is similar to most continental shelves in that it receives runoff from the adjacent land and is bordered on its deep ocean side by a strong boundary current (Gulf Stream). The hydrographic and chemical characteristics of a typical transect across the shelf are shown in Fig. 2. Middle shelf regions are poor in nutrients, whereas the inner shelf receives inputs from river runoff. Upwelling or intrusions from the Gulf Stream, which occur along the entire South Atlantic Bight (1), supply nutrients to the outer shelf.

---

*This research was supported by Grant E(38-1)890 from the U. S. Energy Research and Development Administration.

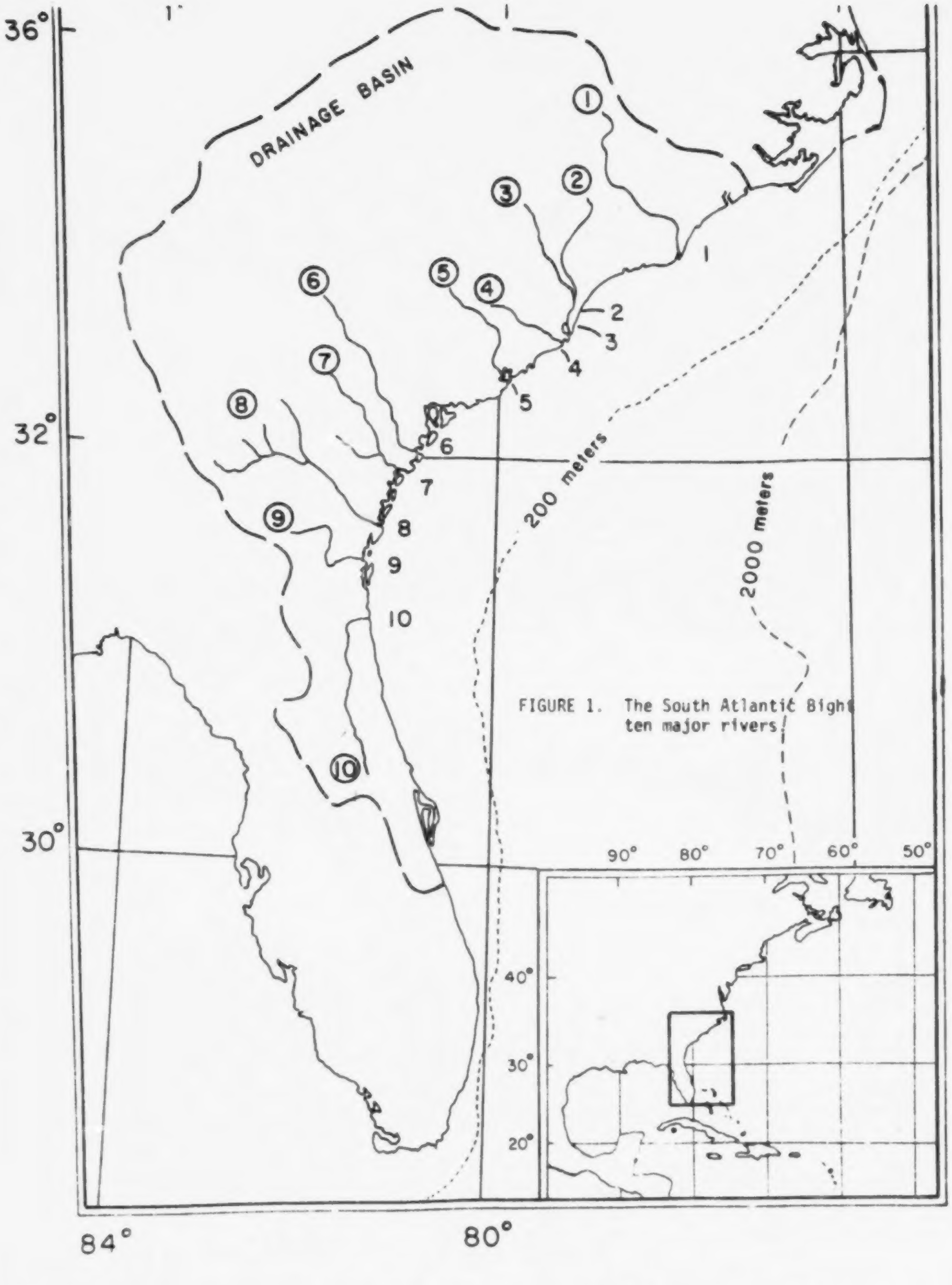


Figure 1. The South Atlantic Bight and its 10 major rivers.

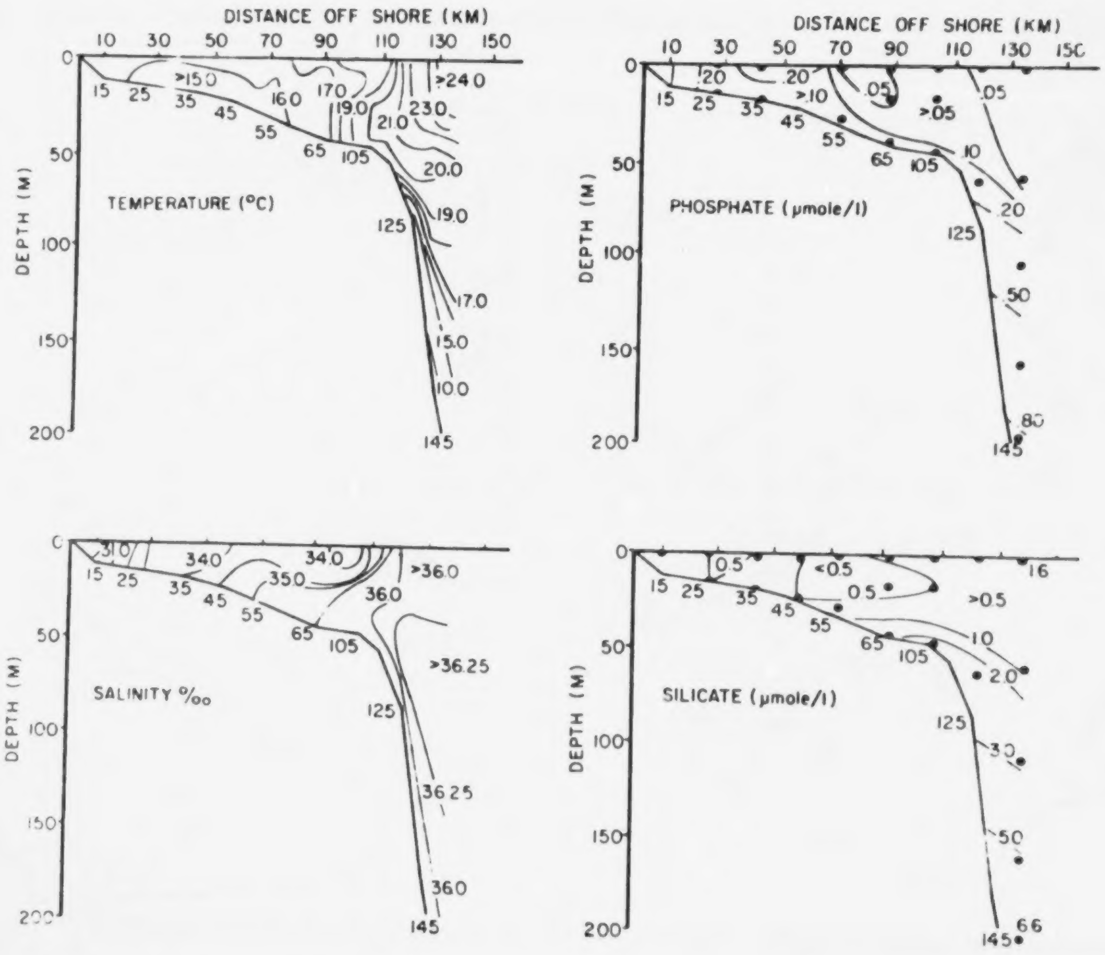


Figure 2. Hydrographic and chemical characteristics along a cross-shelf transect.

Trace elements can be delivered to continental shelves by runoff, atmospheric transport, and onshore intrusions of deep off-shelf waters (Fig. 3). By determining the magnitude of the trace element fluxes to continental shelf waters and comparing it to their total concentrations, it is possible to calculate their residence times. The residence time then can be compared to that of the water (both from intrusions and runoff) to determine whether the elements behave conservatively.

Trace Metal Fluxes to Continental Shelf Waters

Rivers--Ten major rivers discharge into the South Atlantic Bight and are responsible for the major portion of continental runoff. These drainage basins are a mixture of crystalline igneous and metamorphic rocks and sedimentary deposits. In general, each of the five trace elements studied do not vary considerably in concentration from river to river (Table 1). Observed variations probably relate to differences in the composition in the drainage basins.

Only the dissolved phase of trace elements transported by rivers is important to the continental shelf since the suspended load is deposited in estuaries (6, 11). The dissolved components of arsenic, copper, and mercury have been shown to be conservatively mixed through the estuary (9, 10); nickel and zinc probably behave similarly. The conservative nature of these elements during their transit through the estuary probably depends on their chemical form. For example, arsenic in river waters primarily exists in the As(V) form and is associated with low molecular weight organic matter (9). Copper also appears to be complexed with organic matter. Nickel and zinc may behave similarly but little is known of the form of mercury in estuaries.

Assuming that trace elements carried in solution by rivers is conservatively mixed through the estuary, the total river input to the continental shelf can be determined by summing the products of the mean concentrations of the elements for each river and its discharge (Table 2). From these calculations the relative importance of river transport for the trace elements considered is Ni>Zn>Cu>As>Hg, which is the same general order as their relative abundances.

Atmospheric Transport--Because of their proximity to the continents, continental shelf environments may receive significant trace element inputs due to atmospheric transport. Although it is difficult to measure atmospheric trace element inputs directly, their atmospheric concentrations have been used to deduce input rates (4).

Atmospheric concentrations of the five trace elements over the continental shelf of the South Atlantic Bight each vary by about an order of magnitude (Table 3). Much of this variation is undoubtedly due to the trajectory taken by the air parcel sampled. Air transported directly from the continents during offshore winds would clearly be expected to have higher concentrations than that transported during easterly or onshore winds. Some of the variations in atmospheric trace element concentrations may also be due to exchange of trace elements from sea surface to the air (4). Even with these uncertainties, however, the mean atmospheric concentrations of the trace elements

TABLE 1. GEOMETRIC MEAN RIVERINE TRACE ELEMENT CONCENTRATIONS FOR SOUTHEASTERN UNITED STATES

	In solution				
	µg/ℓ[1]				ng/ℓ[1]
River	As[2]	Cu	Ni	Zn	Hg
1. Cape Fear	0.39 (0.16-0.60)	1.6 (0.1-3.1)	8.0 (4.0-15)	6.2 (2.9-8.0)	24 (14-36)
2. Pee Dee	0.21 (0.08-0.32)	1.2 (0.1-2.5)	3.6 (2.2-5.8)	3.7 (1.6-4.8)	20 (10-35)
3. Black	0.36 (0.15-0.57)	1.5 (0.2-2.1)	5.8 (3.0-11)	5.2 (2.3-7.9)	20 (10-38)
4. Santee	0.15 (0.04-0.31)	1.5 (0.4-3.9)	4.0 (1.4-8.0)	4.0 (1.4-6.2)	18 (8-38)
5. Copper	0.27 (0.12-0.47)	1.9 (0.9-3.4)	5.0 (1.4-11)	2.7 (0.6-5.1)	18 (8-28)
6. Savannah	0.30 (0.13-0.47)	1.5 (0.4-3.6)	3.9 (1.0-16)	4.0 (0.5-8.9)	21 (12-38)
7. Ogeechee	0.25 (0.08-0.45)	1.1 (0.2-2.0)	4.1 (1.0-7.5)	2.8 (1.1-4.8)	19 (10-36)
8. Altamaha	0.21 (0.04-0.47)	1.5 (0.3-3.4)	2.7 (1.8-3.2)	3.2 (1.6-6.0)	19 (10-34)
9. Satilla	0.38 (0.25-0.52)	0.9 (0.1-2.6)	2.6 (0.7-3.5)	7.5 (0.7-13)	19 (10-33)
10. St. John	0.49 (0.26-0.72)	1.3 (0.1-2.6)	2.4 (1.6-3.4)	5.9 (1.2-10)	39 (16-61)

[1] range given in parentheses

[2] from Waslenchuk (9)

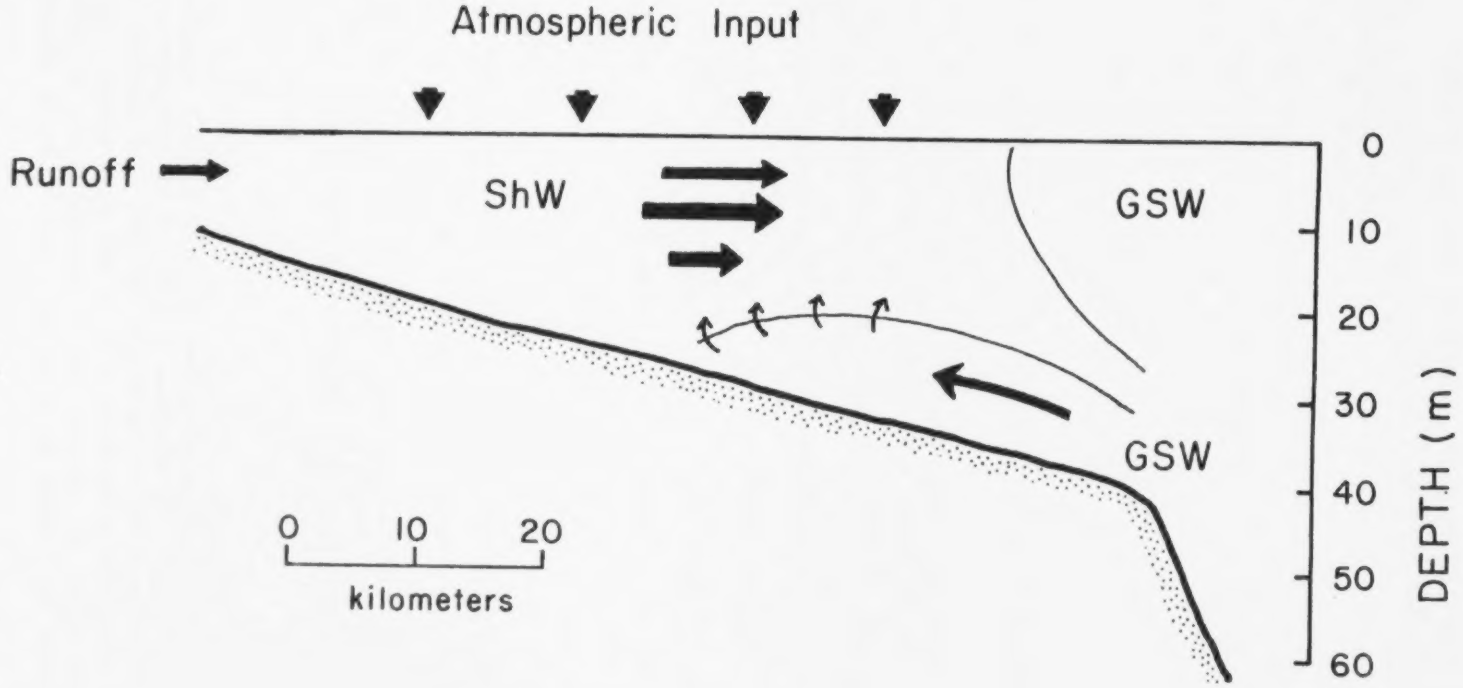


Figure 3. Schematic representation of trace element inputs to continental shelf waters.

TABLE 2. ESTIMATED ANNUAL RIVER TRANSPORT OF TRACE ELEMENT TO THE SOUTH ATLANTIC BIGHT

Element	River transport (kg/yr)
Arsenic	1.4×10^4
Zinc	2×10^5
Nickel	2.2×10^5
Copper	8×10^4
Mercury	1.1×10^3

TABLE 3. GEOMETRIC MEAN ATMOSPHERIC TRACE ELEMENT CONCENTRATIONS AND INPUT TO CONTINENTAL SHELF WATERS[1]

Element	No. of samples	Mean ng/SCM	Range ng/SCM	Annual input[2] (10^5 kg)
AS[3]	11	1.6	0.2-6.3	0.2
Zn	17	8.9	3.4-24	2.9
Ni	17	1.4	0.2-4.8	0.4
Cu	17	3.0	1.0-16	0.9
Hg	42	2.1	0.3-7.6	0.6

[1] Samples collected during summer and winter cruises.

[2] Using a dry deposition velocity of 0.26 cm/sec for As, 0.56 cm/sec for Zn (Cumbray et al., 1975), and 0.5 cm/sec for Cu, Ni, and Hg, and assuming the total atmospheric flux is 3 times the dry fallout.

[3] Waslenchuk (9)

from air samples collected in the summer and winter can be used to ascertain their annual input. Duce et al. (4) proposed a model that utilizes observed dry deposition velocities for trace elements and to take into account washout, assumes that the total atmospheric flux is 3 times the dry fallout. With this model, the trace element input due to atmospheric transport can be calculated for the entire continental shelf area (6×10^4 km^2) of the South Atlantic Bight (Table 3).

Input due to Intrusions--The intrusion of deep Gulf Stream water onto the shelf occurs frequently in the South Atlantic Bight. Details of these intrusions have been described by Blanton (1). Along a given transect of the continental shelf, intrusions occur about 13 times a year (Blanton and Atkinson, personal communication). The intrusions are identified by nutrient concentrations, salinity, and temperature; each excursion apparently displaces 1/5 of the shelf volume. The South Atlantic Bight continental shelf has a volume of 1,920 km^3. Thus, the annual volume of intruded waters to this area is 4,980 km^3.

The intrusions originate in the deep slope waters adjacent to continental shelf and show elevated concentrations of the trace elements (Table 4). The enriched trace element concentrations are apparently due to physical transport of plant and animal detritus from the euphotic zone with subsequent degradation and release of trace elements at depth. This process has been described in several studies of deep ocean environments (2, 7, 3).

An estimate of the annual input of trace elements due to intrusions can be made by multiplying the volume of intruded water by the concentrations of the trace elements (Table 4). It is clear from this calculation that intrusions are the major mechanism of trace element transport to the continental shelf environment.

TABLE 4. ESTIMATE OF TRACE ELEMENT CONCENTRATION AND ANNUAL INPUT IN INTRUSIONS

	Concentration in intrusion waters	Annual input (10^6 kg)
Arsenic[1]	1.5 μg/ℓ	7.5
Zinc	0.61 μg/ℓ	3.0
Nickel	0.61 μg/ℓ	3.0
Copper	0.26 μg/ℓ	1.3
Mercury	25 ng/ℓ	0.1

[1] Waslenchuk (1977)

Trace Element Concentration and Residence Times in Continental Shelf Waters

The concentrations of trace elements in continental shelf waters vary relatively little with depths and seasons (Table 5). Most of the As is in the As(V) form with minor amounts existing as As(III) or dimethyl arsenic acid (9). Little is known of the form of the other trace elements, but the relatively high apparent complexation capacity of continental shelf waters suggests that they may exist as complexes.

TABLE 5. TRACE ELEMENT CONCENTRATIONS IN CONTINENTAL SHELF WATER

	Mean and standard deviation	Total content[1] (kg)
Arsenic[2]	1.04 ± 0.19 μg/ℓ	2×10^6
Zinc	0.49 ± 0.08 μg/ℓ	9.4×10^5
Nickel	0.49 ± 0.06 μg/ℓ	9.4×10^5
Copper	0.16 ± 0.07 μg/ℓ	3.1×10^5
Mercury	20 ± 5 ng/ℓ	3.8×10^4

[1] Assuming continental shelf area of 6×10^4 km^2 and an average depth of 32 m.

[2] Waslenchuk (9)

TABLE 6. RESIDENCE TIME OF TRACE ELEMENTS IN CONTINENTAL SHELF WATERS

Element	Residence time (yrs)	Excess (mg/m^2)
Arsenic	0.27	13
Zinc	0.27	6
Nickel	0.29	4.3
Copper	0.22	3.5
Mercury	0.24	0.35

Of the five trace elements studied, only arsenic appears anomalous in that its excess cannot be reasonably accounted for by the three possible removal mechanisms. As mentioned earlier, uncertainties in the data used for these calculations are probably quite significant, particularly the uncertainty in the determination of the concentration of trace elements in the intruded waters. Our lack of detailed knowledge of the periodicity and volumes of these intrusions may be the severest limitation on this approach. Even so, the above discussion can give considerable insight into the relative importance of processes that govern trace element concentrations and fates in continental shelf environments.

The mean residence time of a given trace element in continental shelf waters can be determined by the following equation:

$$T = \frac{CV}{I_r + I_a + I_i}$$

Where C is the mean trace element concentration, V is the shelf water volume (1,920 km^3) and I_r, I_a, and I_i are the annual inputs due to runoff, atmospheric transport, and intrusions, respectively. Data from Tables 2 through 5 can be used to calculate the residence time for each of the five trace elements. The residence times thus obtained (0.22 to 0.29 yrs.) are remarkably similar (Table 6), but are significantly different from that calculated for water (0.37 yrs.). If the trace elements behave conservatively, their residence time should be similar to that of water. The fact that all trace elements are less implies that an excess amount of each element is transported onto the shelf, compared to that carried off. Even though the uncertainties in the data used may be considerable, it is of interest to calculate this excess (Table 6) to evaluate possible processes that may result in losses in trace elements from shelf waters.

Sedimentation on the shelf is clearly a process of potential importance in the removal of trace elements from the water column. The average shelf sedimentation rate of the South Atlantic Bight is probably something less than 0.1 mm/yr. This value can be used as an upper limit to calculate potential sedimentation losses of these elements. Assuming the sediment accumulating has a trace element concentration similar to average carbonate sediments (8), and a density of 2.0 g/cc, the annual trace element loss would be 0.2, 7, 6, 6, and 0.00x mg/m^2 for As, Zn, Ni, Cu, and Hg, respectively. For zinc, nickel, and copper, this process accommodates the excess amount delivered to the shelf calculated from the model described above. For arsenic and mercury, however, it appears to be an insignificant removal mechanism.

Primary production on the shelf is the major source of particulate carbon in this environment. The average annual production for the entire shelf has been estimated at 170 gC/m^2 (5). This would amount to an annual production of approximately 300 g/m^2 of total particulate organic matter. If the organic matter has concentrations of trace elements approximately equal to that of phytoplankton (20 ppm Zn, 10 ppm As, Cu, and Ni and 0.1 ppm Hg), then annually 6 mg Zn/m^2, 3 mg As, Cu and Ni/m^2, and 0.03 mg Hg/m^2 could be removed from the dissolved phase. Assuming the trace elements are not regenerated on the shelf, this removal mechanism could be of significance for all but mercury.

A large portion of the trace elements delivered to continental shelf waters by atmospheric transport may be inorganic particulates. If we assume that all atmospheric input is of this nature, and does not contribute to the soluble trace element content of shelf waters, the amounts of the excesses for which this could account are 0.3, 4.8, 0.6, 1.5, and 1.0 mg/m^2 for As, Zn, Ni, Cu, and Hg, respectively. This mechanism could account for the apparent excesses in zinc and mercury delivered to the shelf.

REFERENCES

1. Blanton, J. 1971. Exhcange of Gulf Stream Water with North Carolina Shelf Water in Onslow Bay during Stratified Conditions. Deep-Sea Res., 18: 167-178.

2. Boyle, E. A., and J. M. Edmond. 1975. Copper in Surface Waters South of New Zealand. Nature, 253:107-109.

3. Boyle, E. A., F. Sclater, and J. M. Edmond. 1976. On the Marine Geochemistry of Cadmium. Nature, 263:42-44.

4. Duce, R. A., G. L. Hoffman, B. J. Ray, I. S. Fletcher, G. T. Wallace, J. L. Fasching, S. R. Piotrowicz, P. R. Walsh, E. J. Hoffman, J. M. Miller, and J. L. Heffter. 1976. Trace Metals in the Marine Atmosphere: Sources and Fluxes. In: Marine Pollutant Transfer, H. L. Windom and R. A. Duce, eds. D. C. Heath, Lexington, Massachusetts, 77-120.

5. Haines, E. B., and W. M. Dunstan. 1975. The Distribution and Relation of Particulate Organic Material and Primary Productivity in the Georgia Bight, 1973-1974. Estuarine Coastal Mar. Sci., 3:431-441.

6. Meade, R. H. 1969. Landward Transport of Bottom Sediments in Estuaries of the Atlantic Coastal Plain. Jour. Sed. Pet., 39:222-234.

7. Sclater, F. R., E. Boyle, and J. M. Edmond. 1976. On the Marine Geochemistry of Nickel. Earth Planet. Sci. Lett., 31:119-128.

8. Turekian, K. K., and K. H. Wedepohl. 1961. Distribution of the Elements in Some Major Units of the Earth's Crust. Geol. Soc. Am. Bull., 72: 175-192.

9. Waslenchuk, D. 1977. The Geochemistry of Arsenic in the Continental Shelf Environment. Ph.D. Thesis, Ga. Inst. Tech. 62 pp.

10. Windom, H. L. 1975. Heavy Metal Fluxes through Salt-marsh Estuaries. In: Estuarine Research (L. E. Cronic, ed.), Vol. 1, Academic Press, 137-154.

11. Windom, H. L., W. J. Neal, and K. C. Beck. 1971. Mineralogy of Sediments in Three Georgia Estuaries. Jour. Sed. Pet., 41:497-504.

THE FLAMELESS ATOMIC ABSORPTION METHOD FOR MERCURY DETERMINATION AND ITS USE IN CONTROLLING ENVIRONMENTAL POLLUTION

N. S. Poluektov and Yu. V. Zelyukova
Institute of General and Inorganic Chemistry of the
Academy of Science of the Ukrainian SSR Odessa Laboratory

Because of the wide use of mercury in industry and agriculture in the last decade, we have seen its presence increase in environmental pollution. The yearly production of mercury from natural sources and industry is now estimated at about 30,000 tons. Therefore, it is necessary to establish some sensitive, selective, and rapid methods of mercury determination for the systematic control of its content in nature, particularly near large industrial centers.

We propose a method developed by the authors of no-flame atomic absorption for mercury determination (1) based on easy passage of mercury from aqueous solution to a gas phase after its reduction to metal. Fig. 1 shows a diagram of the device used in our work.

Optical density of mercury vapor, obtained from an analyzed solution by air stream or inert gas after mercury is reduced to metal, is measured at λ=253,7 nm. A tin chloride solution was used originally as the reducer. The possibility of other reducers (sodium stannite, ascorbic acid, formaldehyde) was also investigated. These reducers help to remove some interference that occurs when using tin chloride in acid medium (2 to 4).

Sensitivity of the measurement on criterion 2ζ is equal to 6.10^{-4} meg Hg in analyzed solution with optimal parameters, set by the authors (speed of the air stream, 3 ml per second; analytical cuvette, 50 cm; d, 1 cm; the duration of the measurement, 1 to 2 minutes).

Tin Chloride--When using tin chloride, the majority of metals (K, Mg, Na, Cs, Be, Ca, Ba, Cu, Zn, Al, P , Mo, Ni, Mn, Fe) present in the analyzed solution have no influence on the determination of mercury. The majority of inorganic acids, with a concentration of 2 N, have no influence on the final results. Sulfides, however, have great influence because of formation of the insoluble precipitate, HgS. Metal ions, reduced to the elementary state and reacting with free mercury with formaton of amalgams (Ag, Au, Pt), prevent the transfer of the free mercury to the gaseous state. As determined with the method of the isomolar series, the compounds of selenium and tellurium are present in solution form with mercury selenides and tellurides. The ions of iodine, bromine, and fluorine prevent the determination of mercury.

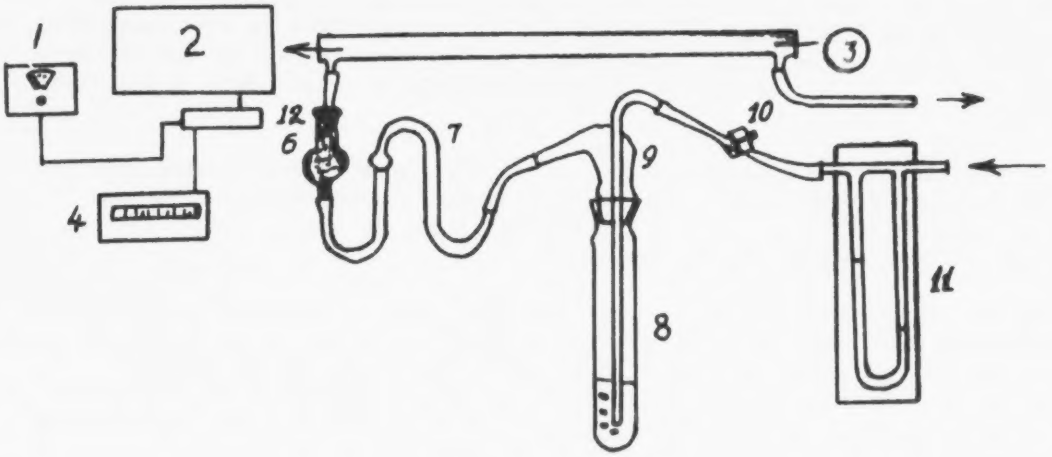


Figure 1. Diagram of the device for mercury determination by the method of atomic absorption in the gas phase: (1) current source FEU; (2) spectrophotometer SF-4; (3) lamp BUV-15; (4) microamperemeter; (5) curvette; (6) calcium chloride tube; (7) trap; (8) test tube; (9) grinded nozzle; (10) clamp; (11) rheometer; (12) photomultiplier.

Ascorbic Acid--As the reducer in mercury determinations, ascorbic acid makes possible the exclusion of the influence of halogens.

Formaldehyde--Reducing mercury does not reduce selenium and tellurium ions, thus making it possible to use this method for mercury determination in selenium and tellurium preparations. The method used corresponds to demands being made for the analysis of environmental pollution. It is widely used in the USSR and abroad (5 to 8). However, certain authors who used this method have described it without referring to our works (9 to 10).

Some of our methods of mercury determination in environment are described below.

Mercury Determination in Natural Water

The above indicated sensitivity of determination is not sufficient for mercury determination in natural waters. We used the rapid method for preliminary concentrating that increases the sensitivity more than two magnitudes of value. Mercury in 1ℓ of water first was reduced with tin chloride. It was then absorbed with a 3 ml 0, 01 N iodine solution by educing from the sample with a stream of inert gas. In its concentrate, mercury was determined, by using a 0.2 ml 10 per cent solution of ascorbic acid as the reducer which was transported as aerozole for bonding of the free iodine vapor. The amount of reduced mercury is equal to 96 or 97 per cent. The minimally discoverable amount of mercury through concentrating one time is 8.10^{-4} meg Hg. Further, increased sensitivity can be achieved from several samples of water by using one absorbing solution. Required time for this analysis is 7 minutes.

Mercury Determination in Air

A method of mercury determination in the air was also developed. It consists of absorbing mercury vapor from air with a 0, 0I n. iodine solution by passing a volume of air through the solution. The absorbing mixture is determined, by using ascorbic acid as a reducer as previously stated.

Required time for this analysis is from 4 to 16 minutes, depending on the mercury concentration in the air.

The outlined methods were used for analysis of natural waters of the northwestern region of the Black Sea to determine human and industrial effluents in the water and atmosphere (11 to 13).

REFERENCES

1. Bazhov, A.S., Ye. M. Yemelyanov, and Yu. O. Shaidurov. 1972. Atomic Abcorbtion Determination of Mercury in Waters of the Atlantic Basin. Isledovaniyev Oblasti Khimicheskikh I Fizicheskikh Metodov Analiza Mineralnogo Syrya (Research in the Field of Chemical and Physical Method for Analyzing Mineral Raw Materials), Issue 2, pp. 186-192.

2. Balashov, A.I., Yu. V. Zelyukova, and N.S. Poluektov. Mercury Content in the Northwest Part of the Black Sea. Okeanologiya, (in press).

3. Vitkun, R.A., Yu. V. Zelyukova, and N.S. Poluektov. 1974. Atomic Absorbtion Determination of Mercury. Zabodskaya Laboratoriya (Factory Laboratory), Vol. 40, No. 8, pp. 949-951.

4. Vitkun, R.A., Yu. V. Zelyukova, and N.S. Poluektov. 1974. Flameless Atomic Absorption Determination of Mercury in Selenium and Tellurium Preparations and the Use of Formaldehyde as a Reducing Agent. Ukrainean Chemical Journal, Vol. 40, No. 12, pp. 1304-1307.

5. Vitkun, R.A., T.B. Kravchenko, Yu. V. Zelyukova, and N.S. Poluektov. 1975. Atomic Absorption Determination of Mercury in Waters. Zavodskaya Laboratoriya, No. 6, pp. 663-665.

6. Vitkun, R.A., N.S. Poluektov, and Yu. V. Zelyukova. 1974. Ascorbic Acid as a Reducing Agent in the Flameless Atomic Absorption Determination of Mercury, Zhurnal Analiticheskoi Khimii, Vol. 29, No. 4, pp. 691-694.

7. Zelyukova, Yu. V., R.A. Vitkun, T.B. Kravchenko, and N.S. Poluektov. 1976. Atomic Absorption Determination of Mercury in Air. Gigiena I Sanitariya (Hygiene and Sanitation), No. 1, pp. 66-68.

8. Poluektov, N.S., R.A. Vitkun, and Yu. V. Zelyukova. Determination of Milligram Quantities of Mercury by Atomic Absorption in the Gaseous Phase. Zhurnal Analiticheskoi Khimii, Vol. 19, No. 8, pp. 937-942.

9. Hatch, W.R.,and W.L. Ott. 1968. Determination of Sub-microgram of Mercury by Atomic Absorption Spectrophotometry. Anal. Chem., Vol. 40, No. 13, pp. 2085-2087.

10. Kirkbright, G.F.,and M. Sargent. 1974. Atomic Absorption and Fluorescence Spectroscopy. Academic Press, London, New York and San Francisco, p. 638.

11. Manning, D.C. 1970. Flameless Methods for Mercury Determination by Atomic Absorption (a Review). Atomic Absorption Newsletter, Vol. 9, No. 5, pp. 97-99.

12. Wilson, A.L. 1974. The Chemical Analysis of Water, London, p. 96.

THE SCIENTIFIC PRINCIPLES OF THE PROBLEM OF SEAWATER POLLUTION

A. I. Simonov and A. N. Zubakina
State Oceanographic Institute
Moscow

The object of scientific study of the problem of seawater protection from pollution consists of development of valid recommendations for the regulation of waste release under which the processes of natural utilization of harmful substances must continuously prevail over pollution. The result should be the elimination, if possible, of disturbances in the marine environment and faults in the ecological system. This definition covers many questions. Some of the more important questions are: 1) the systematic evaluation of pollution of seawaters and its influence on the natural physical-chemical and hydrobiological conditions, 2) studying the ways and parameters of distribution and utilization of pollutants for subsequent definition of the possible regulation of pollutant release into the sea, 3) the development of recommendations on optimal regulations of releasing pollutions in the ocean and sea areas, and 4) prediction of pollutant dynamics of seawaters for present and future perspectives on the set values of waste release and known hydrometerological, hydrochemical, and hydrobiological conditions (6).

The difficulty of making decisions on the above questions is determined, firstly, by the complexity of the subject itself as it touches on many areas of living and non-living matter which predetermines the complicated and interdisciplinary character of fields of oceanographical, biological, chemical, geological, climatological,and other sciences. And, secondly, the amount and direction of oceanography demands on the significant developments for solving this problem.

Observations of pollution, starting in 1965, were made systematically in the seas of the Soviet Union by the Hydrometsurvice under the scientific and meteorological guidance of the State Oceanographic Institute. The observations have now spread over many areas of the North Atlantic and Pacific Oceans.

Investigation of pollution in the North Atlantic by the scientific research weather ships Shkval and Musson were made in 1972 and 1974. The main steps of Soviet oceanographic investigations on pollution problems began in 1971 with three successive cruises of the scientific research weather ships Poryv, Shkval, and Vikhr in seawaters adjacent to Europe (3,7). These observations allow us to make some extremely important conclusions on the nature of the phenomenon itself, and on the pollutant's influence on the substantive composition of seawater.

The most important conclusion from these investigations is that pollution has a global character. At present the most dangerous pollutants are oil, oil products, compounds of heavy metals, mercury, lead, and the pesticides DDT, DDE, DDD, and HCH. According to the International Convention on the Prevention of Seawater Pollution by wastes and other harmful substances, adopted in 1972, these pollutants are prohibited in general from being released in the sea, but are observed equally in interior waters and even in some areas of the open ocean. The pollution fields, as a rule, are generated near the coasts, but spread far from the boundaries of the coastal areas, covering many seas. They are stable in time and space.

Releasing pollutants, on the one hand, results in decreasing oxygen production and, in some cases, in decreasing intensity of oxidation of organics. On the other hand, a sharp decrease in oxygen content that is spent on the oxidation of organics is noted. In semi-enclosed seas (e.g. the Baltic Sea), pollution results in a strong deficiency of oxygen, and in the complete absence of oxygen in lower layers. In open tidal seas, however, (e.g. the North Sea), an oxygen deficiency is also observed. This, in turn, results in accumulation of intermediate oxidation products, such as ammonium. In the Baltic Sea the ammonium content is sometimes more than 30 to 40 years old (6).

Another important conclusion from these investigations is the finding of a significant influence of chemical pollution on the primary production of oceanic waters. It is known that the warm waters of the Gulf Stream are characterized by relatively low productivity. It was confirmed by samples obtained during the Musson cruise that chlorophyll is distributed in the surface layer. In the open ocean, chlorophyll content was insignificant, varying from 0 to 0.05 g/ℓ, in general, and only now and then rising to 0.1-0.2 g/ℓ (in waters of the North Atlantic current). With such a level of primary producation it is practically impossible to understand the degree of influence of chemical pollution on chlorophyll.

In the area of the North American continental shelf, the chlorophyll content was noticeably higher (0.1-1.0 g/ℓ). Estimating the influence of chemical pollutants on the primary productivity of surface waters, it should be noted first, that in the southern part of this area, where mercury concentrations were small, the maximum concentrations of chlorophyll were observed. Pheophytin (its degradation product) was completely absent. This is likely the indication of the pollutant's effects on the primary production of phytoplankton during vegetation.

In the northern part of this area, including Georges Bank, where seawater was most polluted by mercury, oil products, and detergents, the chlorophyll content was considerably lower (generally to 0.1 g/ℓ), but the pheophytin content was sharply increased (to 2-3 g/ℓ). The high concentrations of the chemical pollutants do not inhibit and depress the photosynthesis process in weeds as they ruinously influence living organic matter generated during this process. It is clear that pheophytinization takes place under common conditions; also it takes place during natural dying off of the living cells of phytoplankton. In some areas, as on the Georges Bank, it can take place only during an extremely unfavorable phenonema for plankton production such as heavily polluted waters. The process of chlorophyll degradation and pheophytin formation was much more intensive in Man Bay.

So, the fact that chemical pollution significantly influences seawater's primary production can be considered true.

Finally, the third very important conclusion relates to the role of the main circulation systems and relatively stagnant areas of the seas and oceans in the transport and accumulation of pollutants.

For example, consider the system of the North Atlantic current. It should be noted that it plays an extremely important role in the transport of oil products and other pollutants and that its currents, being saturated near the coasts of North America and Europe, have some relief areas. These include the Sargasso Sea, the Barents Sea, and, likely, also the Norwegian Sea. So, the relatively stagnant areas become gigantic accumulators of harmful substances (7).

The identification of the global character of seawater pollution suggests the importance of clear determination of perspectives for subsequent investigations and development of a global system of observations of seawater pollution. While improving the system of pollution observation, great attention should be paid to the questions of self-purification, the calculations of pollutant balance, and development of recommendations on regulation of optimal conditions for dumping pollutants.

The diagram of pollutant balance can be briefly and quantitatively expressed as follows (6):

$$\Delta Ct = (CM - C'M')[V + (M - M')] = [(C_1m_1 + C_2m_2 + C_3m_3 +$$

$$+ C_4m_4 + C_5m_5 + C_6m_6 + C_7m_7) - (C'_3m'_3 + C'_4m'_4 + C'_5m'_5 +$$

$$+ C_6m_6 + C_8m_8 + C_9m_9)] : (V + \Sigma m).$$

In this equation, unknown components of income and outflow of pollutants can be added to the right side:

ΔCt - is increasing the pollutant concentration for the period of time in the sea, or its part with water volume V;

CM and C'M' - is the quantity of incoming pollutant from all sources and utilized in different ways, where C and C' are the concentrations, M and M' are the water volumes by which the pollutants are transferred through the sea boundaries or its parts;

C_1m_1 - the amount of pollutant coming from the shore, ($C_1m_1 = C_{1.1}m_{1.1} + C_{1.2}m_{1.2} + C_{1.3}m_{1.3} + C_{1.4}m_{1.4} + C_{4.5}m_{1.5}$, the right side of which reflects, correspondingly, the pollutants being added by river systems, dumped from the shore, discharged by sewer systems from the towns, flowing in from storm runoffs and by tidal action;

C_2m_2 - the pollutant quantity, incoming from mining on the shelf ($C_{2.1}m_{2.1}$), from the oil drilling platforms ($C_{2.2}m_{2.2}$), from transportation losses ($C_{2.3}m_{2.3}$), and from discharge water from ships ($C_{2.4}m_{2.4}$);

C_3m_3 and $C_3'm_3'$ - inflow (outflow) during water exchange between the seas;

C_4m_4 and $C_4'm_4'$ - inflow (outflow) of pollutants at the air-water interface;

C_5m_5 and $C_5'm_5'$ - inflow (outflow) of pollutants at the interface of solutions and on suspended particles ($C_{5.1}m_{5.1}$), and with organisms ($C_{5.2}m_{5.2}$);

C_6m_6 and $C_6'm_6'$ - dynamical inflow (outflow) of pollutants from one area into another; $C_6m_6=C_{6.1}m_{6.1}+C_{6.2}m_{6.2}+C_{6.3}m_{6.3}+C_{6.4}m_{6.4}$, where the right side correspondingly reflects inflow with advection, turbulence, organisms, and ice.

C_7m_7 - pollutants incoming as an intermediate product of degradation of other pollutants;

C_8m_8 - pollutant decrease under the chemical and biological degradation;

C_9m_9 - pollutant decrease accumulated in hydrobionts.

The following conditions should be imposed to equate for the variations of environment:

$$0 < C < I\ LPC \qquad \text{and} \qquad \Delta C \leq 0,$$

where LPC is the limited permissible concentration of pollutant.

If this equation is solved relative to pollution of an ocean or sea, as a whole, the terms C_6m_6 and $C_6'm_6'$, reflecting the dynamical redistribution of pollutants between individual areas, can be omitted.

With this balance diagram in mind it is possible to point out the main direction of further investigation, related to development of scientific principles and an observational system of pollutant dynamics. Let us consider these questions, applying them in general to oil and oil products as the most widespread of pollutants.

During study of the balance of components of oil pollution, it becomes evident that the calculation of their input by different ways is most time-consuming. The ways and means of harmful substance input can be direct and indirect.

The direct means of oil and oil product input includes the leakage or catastrophic release during drilling on the shore or shelf, transport accidents, discharge of washing waters and wastes from oil refining and reproducing plants into the sea. Generally, it is possible to test and assess the discharge of wastes, including oil products and leakage of oil, during drilling. It is not difficult from a scientific standpoint. Assessment of catastrophic spills of oil during drilling and transportation should be based on statistical data.

Studying and assessing oil and oil product input by indirect ways, (i.e. from river systems, channels, from the atmosphere, and so on) which are likely the most powerful sources of sea water pollution, is another matter.

The methodical principles of studying the discharge of oil pollution through river systems are, firstly, that oil and oil product concentrations, unlike the natural components of chemical composition, do not depend on the value of total water runoff. Secondly, that the maximum oil pollution discharge must correspond to the time of the greatest storm runoff and surface water flow. This requires systematic observations of oil pollution concentrations dynamics at the heads of deltas and in the outlets of the delta branches. In determining the sampling frequency, it is necessary to take into account that oil, and any other pollution, can be discrete in time and in space. Thus, sampling should be made frequently on the whole river cross section.

Thus, organization for observations of oil pollution discharge by river systems is time-consuming and expensive. Because of this, reliable information on the rates of these discharges is not available in source literature. At the same time, judging by the regular infrequent observations made on some rivers, oil pollution inflow by river is one of the valuable components of the input part of the balance. So, an approximate calculation shows that in the Black Sea, river runoff brings 28.7 per cent of oil pollution annually (including 23 per cent from the Danube).

The calculation of input, and removal of pollutants during water exchange between the seas, can also make up a considerable part of the input part of sea pollution balance. So, in the Black Sea, the inflow of oil pollution, through the channels, is equal to 12.8 per cent of the whole inflow, including 4.2 per cent through the Kerch Channel, and 8.6 per cent through the Bosphorus. In the Baltic Sea, 15 per cent of hydrocarbons of oil origin annually come through the Denmark Channels.

The examples given above reveal the serious importance of the streamflow and the water exchange as a method of significant pollution of a semiclosed sea. It can be seen that inflow of oil pollution by rivers and channels exceeds 40 per cent of the total income.

Naturally, the question arises, by what ways do the rest of the 50 to 60 per cent pollution reach the sea? As mentioned above, they can reach the sea directly. But this result would include the input from the atmosphere. Unfortunately, the estimate of this input was not made, either experimentally or theoretically, in a scientific way. Some theoretical or numerical calculations, insufficiently confirmed by experiments, probably give extremely overestimated results. For example, according to the data of American investigators, the transfer from the atmosphere to the ocean is estimated at ten millions of tons annually. The calculations of oil product input from the surface of the Black Sea, made on a small series of determinations of oil hydrocarbons in the precipitations, probably gave an overestimated value. This inflow was equal to 37 per cent of the total input of pollutants. Comparison of input and expenditure of the pollution balance for the Black Sea, including the inflow from the atmosphere, suggests that input exceeds the expenditure by more than 30 per cent. Under these conditions, two alternatives can be assumed: either the inflow of volatile fractions to the atmosphere balances their inflow (which is unlikely) or there are serious methodical mistakes in determination of pollution inflow from the atmosphere.

It seems, therefore, that investigation of oil pollution balance should be made simultaneously in three directions:

1. The integral estimate of the destruction processes and inflow of pollution on the dynamics of pollutants level, including destruction rate.

2. Studying of pollution inflow by river systems and inflow-outflow through the channels to differentiate the input components in calculations of the above.

3. Studying the inflow-outflow of the sea surface for the same purpose.

The balance, connected with natural utilization of pollutants, is the most difficult problem. Solving of pollution balance is generally impossible without understanding of mechanisms and rates of their degradation. These depend on many factors, and should be investigated at the same time in laboratories and in the field (4,5).

It should be noted that the oxygen content, the temperature conditions, etc., greatly influence the degradation rate of oil products and other pollutants. With an oxygen deficiency, and the temperature below 10° to 15°C, the degradation rate decreased sharply and the accumulation process prevailed over oil product degradation. This situation can be illustrated by the variations of oil product content in the waters of an interior sea (Fig.1). It is characteristic that during two months (April to June) the oil product content decreased by 67 per cent; then, from June to August, the degradation rate decreased but the oil concentration decreased by only 13 per cent. As a whole, the oil product content decreased 80 per cent from April to August. This suggests the significant capacity of the sea for selfpurification. But, in October, when the water temperature and degradation rate decreased considerably, the oil product content began to rise.

The analyses of the experimental data and field observations allow us to express, in rough approximation, the equation of oil product balance as:

$$\Delta Ct = (Ct-1 + \kappa C)e^{-kt};$$

where ΔCt is the increase of oil product concentration for the period of t, and is equal to $Ct-1-Ct$, κC, (increase in the same period of time, including a decrease because of outflow into another sea, and evaporation to the atmosphere), k - the constant of reaction rate.

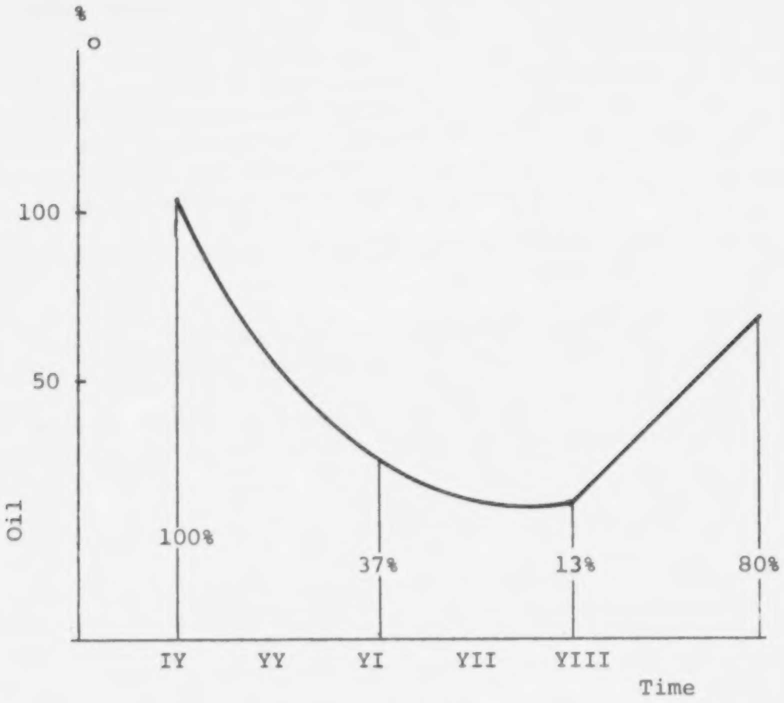


Figure 1. Variations in content of oil products in interior sea.

The balanced equation can be used for calculation of dynamic levels of sea pollution for near and remote perspectives.

It is easy to use and test the calculation diagram, suggested above, on such examples as the North Sea, the Baltic Sea, the Black Sea, and others, under conditions of reliable calculations of mean concentrations of oil and oil products in the whole sea, and in layers. Correctness of the calculation of the ΔCt value can be estimated on the dynamics of mean concentrations calculated from observational data. In this equation the description of degradation kinetics of oil and oil products is the most vulnerable. We shall see below that, strickly speaking, it cannot be approximated by a formal kinetic equation of the first order.

The processes of natural selfpurification are conditioned by hydrocarbon composition of oil and oil products, and specific features of the water basins with different physical-geographical conditions.

The chemical composition of hydrocarbons of oil origin in seawater is the main question in the complex problem of investigation of destruction processes of oil and oil products. Therefore, the main attention of investigators is concentrated on the determination of non-polar and small-polar hydrocarbons.

As our investigations showed, the combination of infrared spectroscopy, gas-chromatography, and fluorescence-indicator methods, allows us to understand the composition of hydrocarbons, separated from the seawater and ice. Experimental investigations made in coastal arctic waters revealed prevailing paraffin-hephthene hydrocarbons in water and ice samples, and a difference between the quality composition of hydrocarbons in ice and seawater sampled at different depths (Fig. 2). It is possible to affirm, that in the ice samples, the maximum peaks of hydrocarbons lies among $C_{17}H_{38}$-$C_{35}H_{72}$, and the traces of light hydrocarbons are marked. On the chromatograms of water samples taken from near the bottom layer, the peak maximum moves to the low temperature area of the chromatogram and includes hydrocarbons $C_{12}H_{26}$-$C_{17}H_{36}$. The concentration of paraffin-naphthene hydrocarbons, obtained by boiling at high temperature, is insignificant.

The presence of light hydrocarbons (cyclohexane, ethylcyclohexane, methylcyclohexane, and nonane) is likely because hydrocarbons with low molecular weight are not especially volatile at negative temperatures.

Information available from present literature is concerned with the composition of n-alkanes in the surface waters of the coasts of Bermuda, the Gulf of Mexico, the Caribbean Sea, East and North Atlantic, the Persian Gulf, the Greenland Sea, the Mediterranean Sea, and the Indian Ocean. Investigations made in the above mentioned areas showed the presence of n-alkanes, generally from C_{14} to C_{37}, with a maximum content of C_{27}-C_{30} in East Atlantic waters, and C_{15}-C_{20} in waters of the Gulf of Mexico. Hydrocarbons in oceanic waters were found to be complicated mixtures, including the saturated and aromatic compounds with the atomic number of carbon in molecules from 14 to 32.

Based on the data of all the above mentioned authors, and taking into account the wide spectrum of molecular weights for hydrocarbons isolated from water and ice, it is possible to determine that the hydrocarbons found originate from oil. As the hydrocarbons, isolated from water, ice, and diesel oil of the survey area, have the same group composition, the diesel oil was taken as substratum for studying hydrocarbon oxygen characteristics. As n-paraffines in diesel oil and seawater samples prevail, ability of oil-oxydizing bacteria to oxidize the mixture of alkanes including C_{10}, C_{12}, C_{14}, C_{15}, C_{16}, C_{19}, C_{20}, C_{24}, and cyclohexane, was studied (1,8).

In investigating the processes of hydrocarbon oxidation, the most attention was paid to a study of the temperature influence (the main factor of chemical and microbial genetics) on their quantitative and qualitative variations. The temperature range of -0.3 to 0.6°C, +2°C, +10°C, +20°C was selected.

Analyzing the results of chemical and bacterial oxidation of hydrocarbons of diesel oil and n-alkanes, obtained at different temperatures, it is possible to affirm that bacterial oxidation of diesel oil by hydrocarbon-oxidizing bacteria, isolated from water and ice, is active at the temperature +20°C. This fact was noted by many investigators in different areas of the world's oceans.

At the same time, at temperatures near 0°C, when chemical oxidation is reduced, the bacterial oxidation of hydrocarbons increases significantly (Table 1). In consideration of the ratio of the chemical and bacterial

TABLE 1. KINETIC CHARACTERISTICS OF THE PROCESSES OF CHEMICAL AND BACTERIOLOGICAL OXIDATION OF DIESEL OIL HYDROCARBONS AND N-ALKANES.

	T°C	C_0,mg	C^∞, mg		oxidation %		K_2, l^{-1}mg-day^{-1}		K_1,day^{-1}		W, day^{-1}		K_1C^∞,mg day^{-1}	
			Chem.	Bacter.	Chem.	Bacter.	Chem.	Bacter.	Chem.	Bacter.	Chem.	Bacter.	Chem.	Bacter.
Diesel Oil	+20	760	700	730	13.2	96	0.015	0.002	0.078	0.036	1.548	1.496	7.8	26.9
	+10	1958	78	985	3.9	50.3	0.012	0.000	0.000	0.177	0.936	0.571	0.031	174.34
	+2	2200	40	780	1.8	35.4	0.003	0.000	0.013	0.033	0.145	0.189	0.52	25.74
	−0.3 −0.6	2.36	0	0.92	0	30.9	0	0.724	0	0.035	0	0.702	0	0.322
n-alkanes C_{12}	+20	60	9	54.6	15	91	0.168	0.018	0.177	0.075	1.609	1.057	1.590	4.09
	+10	45.4		8.9	5.1	20	0	0.066	0	0.026	0	0.614	0	0.231
	+2	92.5		12.5	0	13.5	0	0.015	0	0.114	0	0.300	0	1.425
C_{14}	+20	27.6	8.1	25.5	29	92	0.172	0.035	0.032	0.159	1.42	1.027	0.26	4.050
	+10	14.8		5.3	8.1	35.8	0	0.244	0	0.004	0	0.496	0	0.0081
	+2	33.2		11.2	0	33.7	0	0.017	0	0.020	0	0.210	0	0.224
C_{16}	+20	15.9	4.9	13.9	31	87	0.178	0.10	0.033	0.078	1.86	1.460	0.16	1.080
	+10	12.1		3.1	4.1	25.6	0	0.246	0	0.013	0	0.770	0	0.040
	+2	32.6		7.6	0	23.8	0	0.167	0	0.048	0	0.427	0	0.365
C_{19}	+20	2.7	1.6	2.5	59	92	1.646	0.632	0.003	0.073	2.64	1.650	0.004	0.180
	+10	11.1		6.1	10.7	54.8	0	0.099	0	0.059	0	0.663	0	0.359
	+2	17.8	12.8	17.8	71.9	100	0.045	0.008	0.005	0.078	0	0.23	0	1.388
C_{20}	+20	2.7	1.2	2.5	44	92	1.313	0.508	0.026	0.123	1.60	1.39	0.031	6.01
	+10	2.4		2.4	0	100	0	0.699	0	0.064	0	0.905	0	0.154
	+2	13.1	9.1	13.1	69.4	100	0	0.031	0	0.038	0	0.445	0	0.498

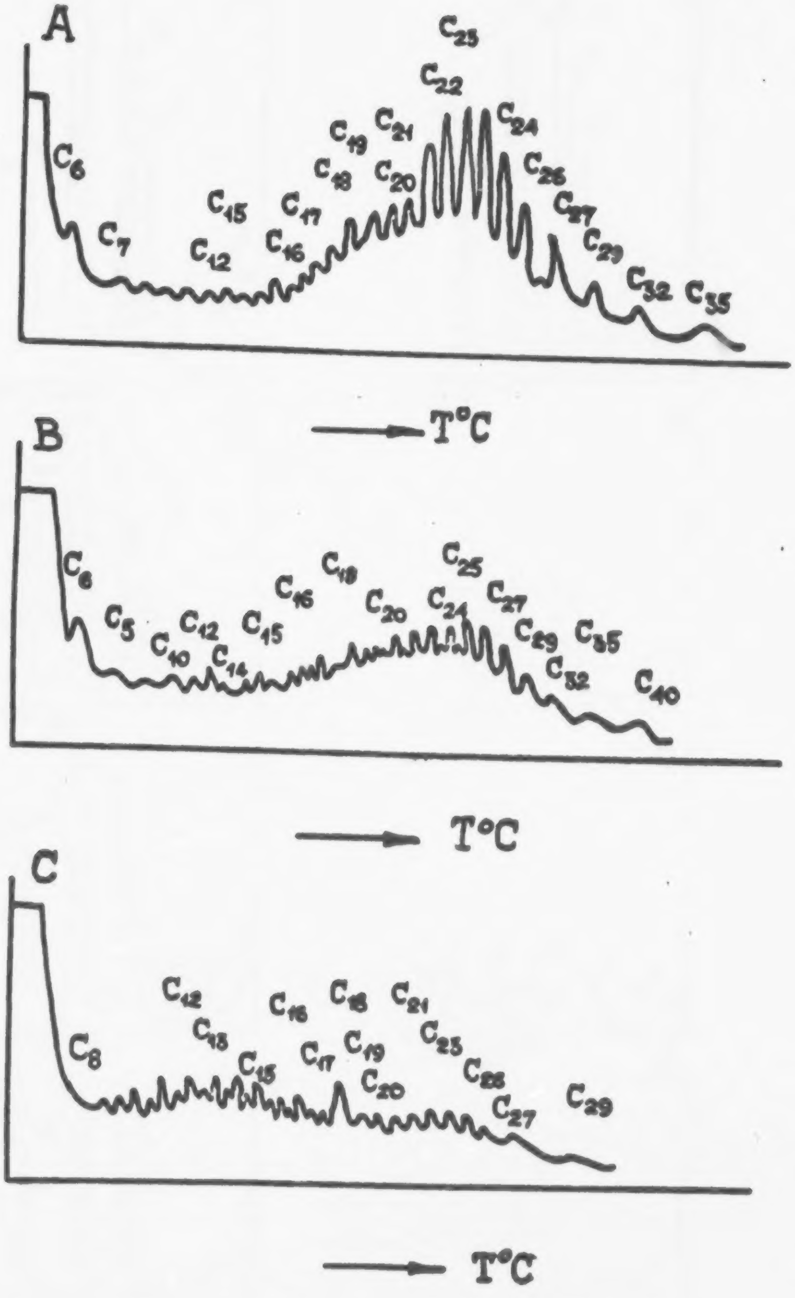


Figure 2. Gas chromatograms of hydrocarbons from ice (A) and water from under-ice (B) and near-bottom (C) layers.

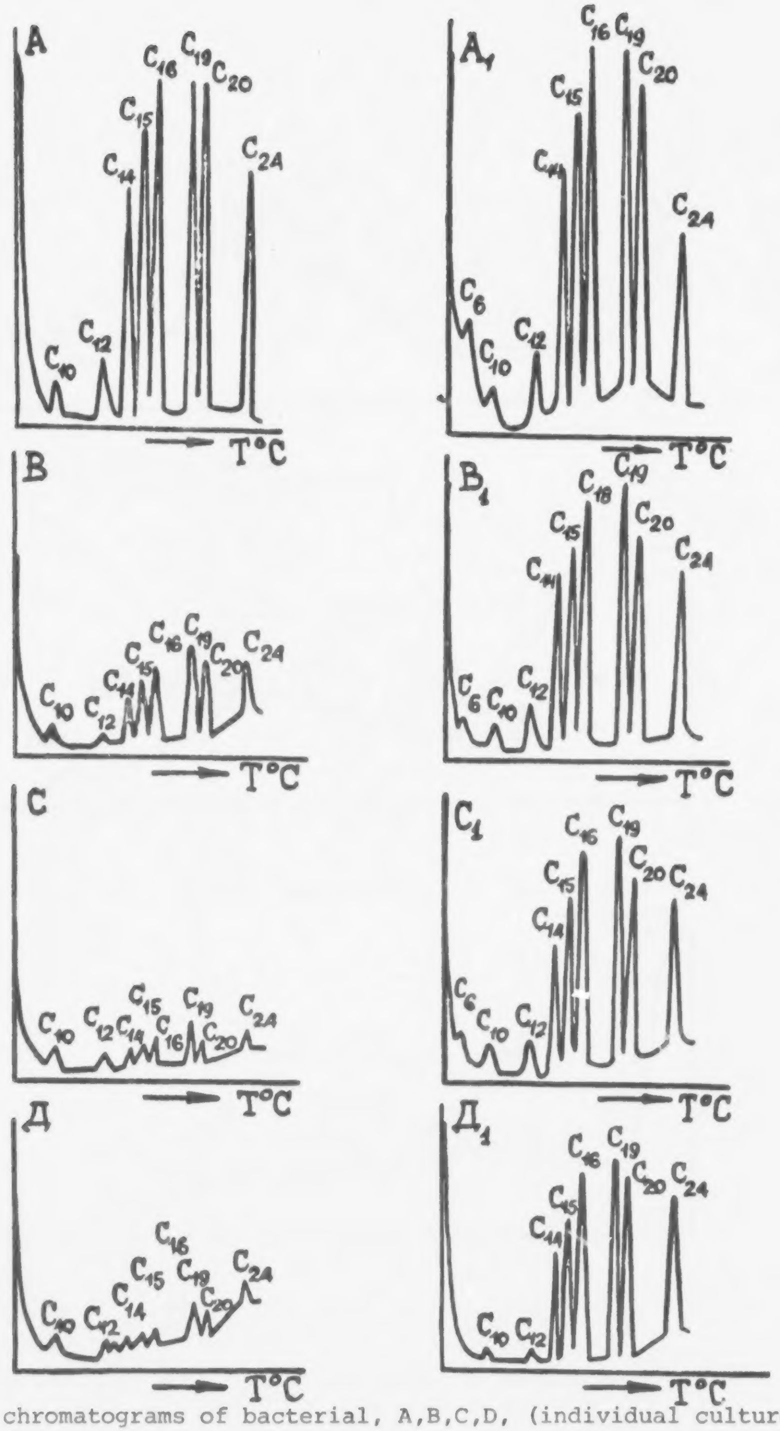


Figure 3. Gas chromatograms of bacterial, A,B,C,D, (individual culture) and chemical, A_1, B_1, C_1, D_1, oxidation of an n-alkane mixture at +20°C. A_1, in 0 hr, A,A_1, in 24 hr, B,B_1 in 48 hr, C,C_1, in 72 hr, D,D_1, in 96 hr.

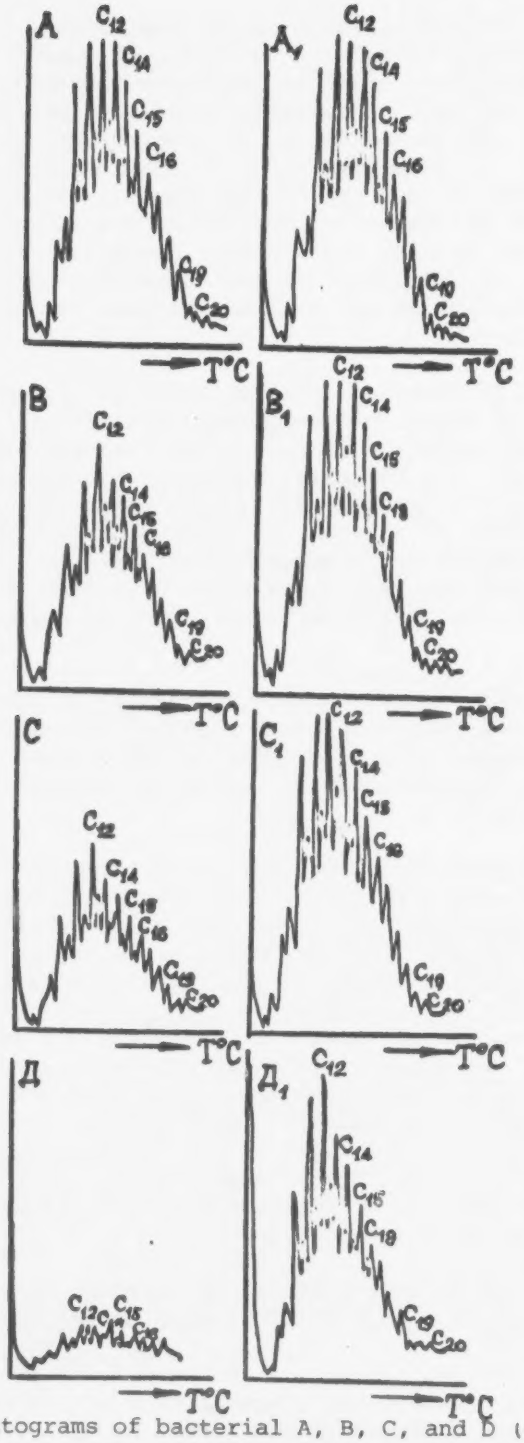


Figure 4. Gas chromatograms of bacterial A, B, C, and D (culture mixture) and chemical A_1, B_1, C_1, and D_1, oxidation of n-alkanes mixtures, at 20°C. A_1, in 0 hr, A,A_1, in 24 hr, B,B_1, in 48 hr, C,C_1, in 72 hr, and D,D_1 in 96 hr.

oxidation of diesel oil hydrocarbons in all experiments made, the original course of the process was revealed. Oxidation of diesel oil is caused generally by bacterial factors, whose role increases gradually with the time of exposure at +20°C. The role of bacterial oxidation processes at +10°C increased sharply on the second day of the experiment, and at +2°C, it decreased sharply on the seventeenth day. Under conditions of destruction of the n-alkanes mixture, the role of the chemical oxidation increased considerably. In almost all cases, on the second day of testing, the portion of chemical oxidation was greater than that of bacterial oxidation. But on the second or fourth day of incubation of the bacterial culture, the indicators of active bacterial oxidation of the n-alkane mixture were much higher than that of chemical destruction.

In a comparison of kinetic characteristics of processes of chemical and bacterial oxidation of diesel oil n-alkanes at different temperatures, the activity of bacterial oxidation of individual n-alkanes at any one temperature was not observed. The bacterial and chemical degradation shows some electivity between the adjacent terms of homologous series of n-alkanes. This selection depends, first of all, on the hydrocarbon ratio of other homologous series (olefines, aromatic hydrocarbons), available in the samples examined. It becomes evident that for laboratory study of hydrocarbon oxidation processes in any marine area, the correct selection of oxygen sources is of great importance.

The bacterial oxidation of n-alkanes affects the samples and influences the substratum to a greater extent than chemical oxidation and has a greater influence of hydrocarbons with a low boiling temperature. The variation of n-alkanes under bacterial and chemical oxidation emphasizes the selectivity of bacterial oxidation.

So, in the test with individual cultures, the cyclohexane disappears on the first day of the experiment. The disappearance is explained by availability of n-alkanes. The n-alkanes, being the growth substratum for bacteria, promote bacterial oxidation. The chromatogram is characterized by a decrease in the hydrocarbon peak from $C_{12}H_{26}$ to $C_{24}H_{50}$ on the second day of experiment. Whereas, the peak area, corresponding to $C_{10}H_{22}$, decreases gradually, and, to the end of the experiment, it shows the persistence of decane to bacterial oxidation. Chemical oxidation is revealed most strongly on the second day of $C_{12}H_{24}$ (dodecane), $C_{14}H_{30}$ (tetradecane), $C_{19}H_{40}$ (non-decane), $C_{20}H_{42}$ (eicosane), and $C_{24}H_{50}$ (tetracosane). It is evident from chromatograms that hydrocarbons with a greater molecular weight ($C_{19}H_{40}$, $C_{20}H_{42}$, and $C_{24}H_{50}$) (Fig. 3) are greatly oxidized at all temperatures. This situation doesn't contradict the Jobson et al. (9) data obtained when studying bacterial oxidation of crude oil at the temperature of +4 C.

In a test with the culture mixture, the gradual decrease of peak areas takes place in concentrations of the following normal alkanes during the first three days: $C_{14}H_{30}$, $C_{15}H_{32}$, $C_{16}H_{34}$, $C_{19}H_{40}$, $C_{20}H_{42}$, and $C_{24}H_{50}$. Dodecane ($C_{16}H_{26}$) decreased sharply on the second day of the experiment. Decane ($C_{10}H_{22}$) doesn't change the concentration to any extent. During chemical oxidation, dodecane disappeared completely on the second day of the

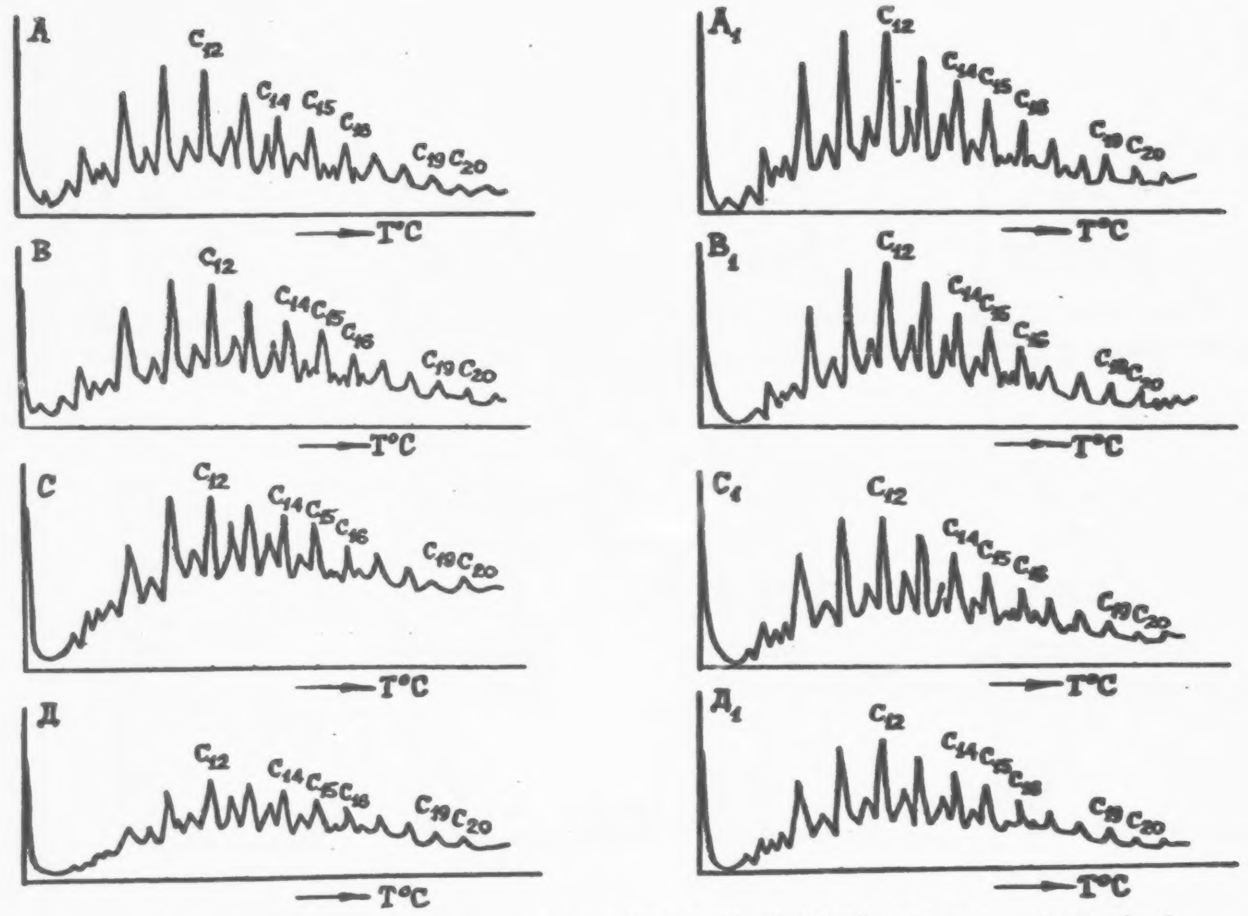


Figure 5. Gas chromatograms of bacterial, A,B,C,D (individual culture) and chemical, A_1, B_1, C_1, D_1, oxidation of diesel oil hydrocarbons at +20°C. A_1 in 0 hours, A,A_1 in 24 hours, B,B_1 in 48 hours, C,C_1 in 72 hours, and A,A_1 in 76 hours.

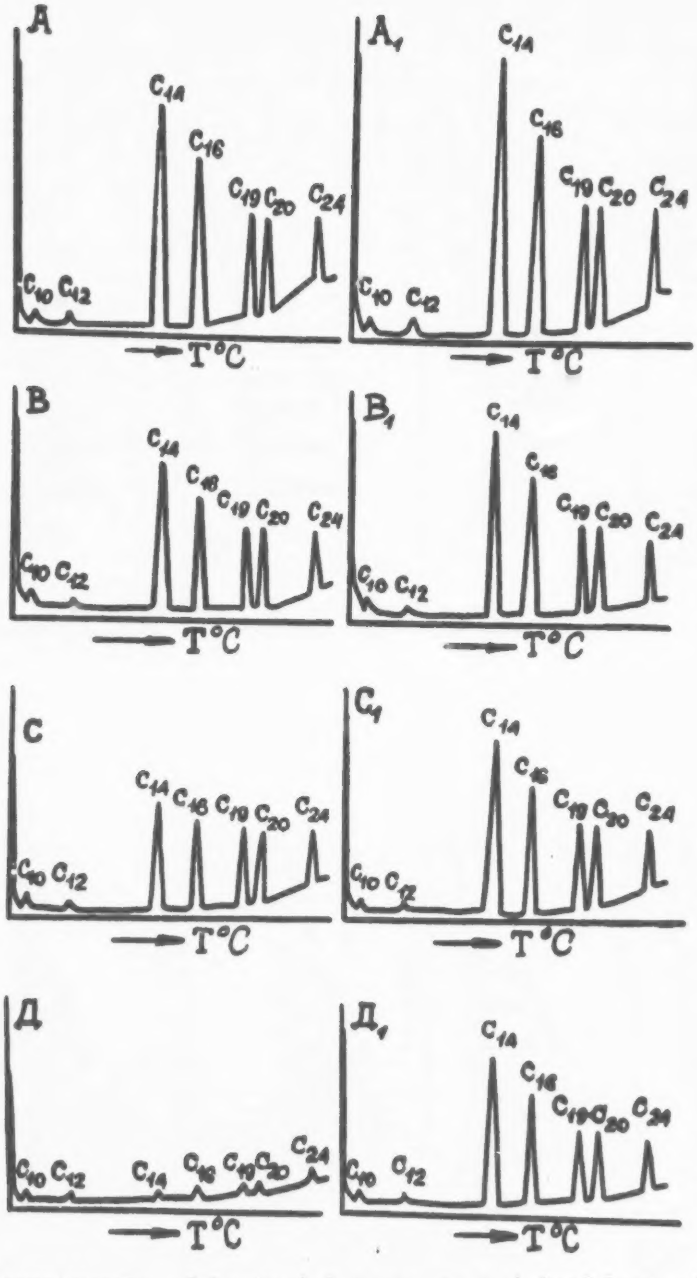


Figure 6. Gas chromatograms of bacterial A, B, C, D (mixed bacterial population) and chemical A_1, B_1, C_1, D_1, oxidation of diesel oil hydrocarbons at +20°C.
A_1 in 0 hr, A,A_1 in 24 hr, B,B_1 in 48 hr, C,C_1 in 72 hr and D,D_1 in 96 hr.

experiment, while hydrocarbons, from $C_{14}H_{30}$ to $C_{24}H_{50}$, disappeared gradually. $C_{10}H_{22}$ content decreased only by approximately 70 per cent on the fourth day, but during the first three days it was not changed (Fig. 4). These data suggest the stability of $C_{10}F_{22}$ against bacterial oxidation.

It can be seen from gas chromatograms, obtained in the experiment to study variation of quantitative composition of diesel oil hydrocarbons by individual cultures and culture mixture of hydrocarbon-oxidizing bacteria, that bacterial oxidation covers hydrocarbons of a large range of molecular weights (Figs. 5, 6). Both the example of n-alkane peaks, identified in diesel oil, and the analysis of kinetic characteristics, show that hydrocarbons of one homologous series are oxidized at the same rate. Experiments show that variation of quantitative composition is determined, firstly, by oxidation of lightly volatile hydrocarbons of small molecular weight. During the first days of the experiment, the principal differences of the processes affecting diesel oil hydrocarbons were not observed. In 24 hours the quantity of normal alkanes decreased relative to compounds that are representatives of other homologous series: napthenes, olefines, and aromatic compounds. It was confirmed by data from fluorescent chromatography, that characterized the variation of group hydrocarbon composition.

On the fourth day of the experiment, n-alkanes with longer hydrocarbon chine, from $C_{16}H_{34}$, to $C_{20}H_{42}$, were oxidizing more actively than n-alkanes with a shorter chain, excluding $C_{19}H_{40}$, which was practically not assimilated at all during the experiment. This change was confirmed by the value of the initial rate of oxidation for $C_{19}H_{40}$, calculated from the kinetic equation and equal to 0.18 mg day^{-1}.

Chemical oxidation is revealed in the concentration variation of hydrocarbon with a low boiling point and simultaneous decrease of all diesel oil hydrocarbons.

At $+10^{o}C$ and $+2^{o}C$, the character of the bacterial oxidation differs considerably from biodegradation at $+20^{o}C$, and it is revealed by intensive oxidation of n-alkanes in series from $C_{14}H_{30}$, to $C_{20}H_{42}$. Analysis of kinetic characteristics shows that the constant of the oxidation rate is practically linear, depending on the number of carbon atoms in n-alkanes.

Chemical oxidation in experiments at low temperatures shows an insignificant percentage and doesn't reveal visual variations of chromatograms.

In general, the analysis of gas chromatograms illustrates the quantitative and qualitative variations and relative oxidation rate of the diesel oil hydrocarbons. It is also the base for the calculation of the kinetic characteristics of hydrocarbon oxidation processes.

As has been pointed out above, the main purpose of the investigation of the destruction process of hydrocarbons of oil origin was made to determine the rate of these processes for subsequent estimates on the possibility of selfpurification, and prediction of the dynamics of pollution levels.

Unfortunately, available data on hydrocarbon oxidation rates are not comparable. The main difficulty of comparing the analysis data from different investigations is in the distinction of methods used for estimating the oxidation processes of oil and oil products. Traditional investigations of bacterial activity by means of studying the quantity and rates of microorganisms generated, measuring the rates of oxygen consumed, carbon dioxide extracted, and determination of decreasing oil concentration in the incubation period, are the most widespread methods used. For estimating the metabolism rate in the process of biological transformation of hydrocarbons, different numerical methods are used.

The kinetic description of hydrocarbon oxidation processes (as in any other organics) is of great importance. In practice, it reflects the complicated picture of interaction between chemical and biological factors. The equation of the first order is frequently used for kinetic calculations of mixture-oxidation in near-bottom waters. Experimental observations show that hydrocarbon oxidation, and oxidation of other organics in seawater, does not proceed at the same rate. It is evident from the analysis of hydrocarbon oxidation dynamics that the process develops intensively in the initial period of incubation. On the other hand, a delay of some days occurs (induction) with the subsequent activation of oxidation. After the incubation period, when there is no marked, analytically fixed oxidation of mixtures, the autocatalitical character of the process is revealed. In such a regime of oxidation processes the first order reaction equation doesn't describe the experimental data for the whole investigation period.

Experimental investigations have found that hydrocarbon oxidation dynamics show S form of process development. The equation of A type (2) is the most convenient for the analysis of this type of curve.

The equation in integral form allows us to calculate the hydrocarbon concentration for the any moment of time. The integral form of autocatalitic equation is:

$$(C) = (Co) - \frac{|B|^{o}(e^{wt}-1)}{1 + \zeta_{o} e^{wt}}. \tag{1}$$

The differential form is:

$$-\frac{|d|c}{dt} = K_k \left(|C_o| - X\right)\left(|B|^{o} + X\right), \tag{2}$$

where (C_o) = initial hydrocarbons content, mg/ℓ.
(C) = hydrocarbon concentration to moment of time, mg/ℓ.
K_k = the rate constant of the second order.
$|B^o|$ = concentration of intermediate products, equal numerically to the ratio K_1/K_k,
X = the quantity of oxidized hydrocarbons, equal to $C_o - C$
where $W = K_k(|B|^{o} + |Coo|)$, $K_1 = K_k\ |B|^{o}$. (3)
Coo = maximum oxidation.
$W_1 K_1$ = the rate constant of the first order, day^{-1}:

The initial rate of oxidation mg/ℓ per day:

$$V_1 = K_1(C\infty) \qquad (4)$$

Investigation of processes of chemical and bacterial oxidation of diesel oil hydrocarbons and n-alkanes in diesel oil under different temperature conditions allowed us to determine the influence of temperature on the kinetics of bacterial and chemical oxidation of n-alkanes. The validity of one of the most important temperature characteristics, E, the activation energy, was estimated by kinetic characteristics obtained under different temperature conditions for diesel oil hydrocarbons.

On the basis of all the kinetic calculations of the rate constants for bacterial and chemical oxidation of diesel oil hydrocarbons and n-alkanes in different hydrocarbon mixtures, the values of one of the most important temperature characteristics, activation energy, were obtained. These values allowed us to calculate the rate constant of oxidizing processes at different temperatures. The kinetic characteristics can be useful for process modeling under field conditions. They also permit an approach to forecasting selfpurification possibilities of marine ecosystems.

Thus, through the example of hydrocarbons of oil origin, we found that the pollutant degradation processes are extremely complex and depend considerably on concrete physical-chemical and microbiological conditions. The pollutants are characterized by their own kinetics and degradation rate under the influence of prevailing processes. Therefore, further efforts should be made to study the parameters characteristic of every category of pollutant. Their transformation and degradation in multicomponent mediums should be described.

The exceptionally large space scale of spreading pollution, the characteristics of its distribution, depending on water circulation, and the condition of degradation, suggest a number of questions to be answered about the problem of pollution in the world's oceans. Among them, the development of a global system of observation of chemical pollution in the marine environment is an initial step in development of a global system of observation of ecological consequences of marine pollution.

Considerations expressed in this article are the elements relating to the scientific principles of development of such a system.

REFERENCES

1. Zubakina, A.N., A.V. Tsyban, S.P. Bariniva, and I.M. Mikhaleva. 1975. On the Role of Physico-chemical and microbiological Factors in the Destruction Processes of Hydrocarbons of Oil Origin. Proceedings of I All-Union Symposium, Oceanographical Aspects of Water Protection from Pollution. M., pp. 66-72.

2. Leonov, A.V. 1974. Generalization, Typification, and Kinetic Analysis of Curves of Oxygen Demand on the BOD-experiments Data. Okeanologiya, T. 14, N.I., p. 82.

3. Oradovski, S.G., A.I. Simonov, A.A. Yustchak. 1975. Investigation of the Character of Chemical Pollution Distribution in the Gulf Stream Area and its Influence on the Primary Productivity of the Oceanic Waters. Meteorologiya I Hydrologiya, N. 2, pp. 48-58.

4. Simonov, A.I., Y.S. Tokuev, and V.S. Chernyshov. 1972. On the Free-radical Reactions of Physico-chemical Processes of Natural Water Self-purification. The Report of VI All-Union Science Conference on Sea Chemistry, AN USSR, M., pp. 55-56.

5. Simonov, A.I., and L.K. Lykova. 1972. Influence of Some Physico-chemical Factors on the Rate of Phenol Destruction in Brackish Waters. Proceedings of IV All-Union Symposium on the Modern Problems of Self-purification and Regulation of Water Quality. Tallin, 25 October, 1972, pp. 34-38.

6. Simonov, A.I. 1973. In: Foreword, Sea Pollution by Oil. L., Hydrometizdat. pp. 5-17.

7. Simonov, A.I., S.G. Oradovski, and A.A. Yustchak. 1974. The Modern State of Chemical Pollution of the North Atlantic Waters. Meterologiya I Hydrologiya, N.3. pp. 61-69.

8. Tsyban, A.V., A.N. Zubakina, V.V. Il'inskij, and S.P. Barinova. 1975. Modelling of Microbial Oxidation Processes of Oil and Diesel Oil. Proceedings of the I All-Union Symposium, Oceanographical Aspects of the Water Protection from Chemical Pollution, M. pp. 191-194.

9. Jobson, S., F. Cook ,and D. Westlake. 1972. Microbial Utilization of Crude Oil. Appl. Microbiol., 23, v.6, pp. 1082-1089.

MONITORING OF MARINE ENVIRONMENT AS AN INFORMATION BASIS FOR ECONOMIC-ECOLOGICAL CONTROL

M. T. Meleshkin, A. I. Simonov, A. M. Bronfman,
V. E. Glushkov, and A. L. Suvorovsky
Economics Institute of the Ukrainian Academy of Sciences
Odessa

Urgent problems arising in developing a long-term strategy of exploiting and protecting the marine environment are part of the general problem known as "man and surrounding medium," and, naturally, these problems should be investigated and solved in conjunction with already known methodological approaches.

It is evident, however, that continuity in this respect cannot be complete because the marine environment, as an object and subject of anthropogenic influences, is remarkable for its specific nature. At the same time, it may be possible to offer a general methodological conception which is equally acceptable when developing a theoretical foundation while retaining measures for nature protection, irrespective of the field of application. To fully attain the objectives mentioned above, in our opinion, it would be wise to use a conception of unity of economy and ecology within which any process of employment of natural environment is considered as an interchange of matter and energy between such subsystems as "economy," meaning the economic activity of man, and "environment" presented by both abiotic and biotic complexes. Insoluble ties between these subsystems unite them into a common economic-ecological system.

The major premises and principles of the proposed conception are outlined below:

1. The scale and rate of modern productive forces are objective factors leading to rapid increase of anthropogenic loads on the biosphere which are comparable with the scale and rate of natural influences. The evaluation and prediction of possible changes because of these factors, as well as the development of control systems for nature protection, cannot be accomplished by conventional isolated methods of economic and ecological analysis. Naturally, a need arises for the development of new qualitative methods for investigation and control based on the knowledge of the laws of behavior of the complicated economic-ecological systems.

2. The methodological basis for determining the irregularities of development of economic-ecological systems should be the consideration of such peculiarities of the natural environment as its inertia, ability for adapting and self-adjustment, and, finally, the probability character of its parameters

and processes.

3. As a basis for economic-ecological planning, use should be made of the principles of staging, and territorial differentiation and complexity, in contemplating the combined use and reproduction of natural resources (1, 2).

4. Solving the problem of optimum interaction in the "economy-environment" system demands a complex approach to controlling the subsystems with the aim of attaining their balanced development. Necessity for such an approach is emphasized by the recently observed processes of intensive mutual penetration of the economy and ecology at the local, regional, subregional, and global levels.

5. Unity of the economy and ecology stems not only from their interrelation, but also from the possibility of attaining some, or other, social aims by the simultaneous controlling of both the economic parameters and the state of the environment.

ECONOMIC ZONING

In the application of our theme, the principal task in controlling the processes of functioning of the economic-ecological system, is the attainment of the necessary conformities in the interchange of matter and energy between economy and the marine environment.

The sea and, especially, oceanic biogeocenoses that have a certain resistance to external influences and considerable capabilities of adapting allow man, within certain limits, to change the conditions of the surrounding medium. However, these changes should not go over the boundaries beyond which breaks the established links intrinsic in biogeocenosis as a system in a state of dynamic equilibrity.

In the present state of social development, the threat of such a situation is real enough. In a large number of water areas, the anthropogenic transformation of the ecological systems is an accomplished fact. Chemical pollution plays a dominant role in this process.

It is well known that the effectiveness of modern production, with respect to utilization of resources, remains at a very low level. A finished article contains, on the average, about 5 to 10 per cent of the raw materials used in its construction (3). The remaining 90 to 95 per cent, in the form of waste, is dumped into the surrounding medium. The greater part of these wastes is being accumulated in the world's oceans, especially in shelf waters and inland seas.

The ever increasing amount of anthropogenic-wastes dumped into the marine environment, and areas connected with it, cause development of unfavorable ecological conditions which sharply increase the problem and the necessity of active and purposeful control of the situation.

Objective control of the complicated, dynamically developing economic-ecological systems can only be accomplished by use of all information allowing developing situations to be predicted, planned decisions to be made, and the criteria of cost, time, effectiveness, and risk evaluated.

The character of the information obtained should also be guided by a program relative to control purposes. Such a program can generally be formulated as bringing anthropogenic influences in agreement with the adapting capacity of the environment.

Reaching such an agreement is a problem of a very complicated nature. Regarding chemical pollution, such an agreement contemplates the forming of balanced economic-ecological systems in which the amounts of toxic wastes from the economic activity of man would be properly rated with respect to the potential detoxicating abilities of the receiving water basins (which, at the same time, would have no harmful effect upon the biogeocenoses). In fact, it would be necessary to rate maximum permissible dumpings (MPD) in considering the marine environment's self-cleaning potential (SCP) and subsequent step-by-step attainment of such quantitative relations between the two which would guarantee a stable content of pollutants at a level not exceeding maximum permissible concentrations (MPC).

The proposed outline of the problem is a further development of the scientific basis of monitoring put forward by Yu. A. Izrael at the First Soviet-American Symposium on Comprehensive Analysis of the Environment (4). This statement of the problem has many points in its favor.

First, it contemplates passing from studying the state of pollution in the marine environment to studying the processes of its dynamics, depending on determining factors. The principal factor is the development of productive forces and the whole complex of characteristics forming the self-cleaning potential of the environment. It is important that the latter circumstance allows respective links between the "economy" and "environment" subsystems to be established. Such subsystems are required for the purpose of control and, particularly, to solve the immediate problem of the most reasonable redistribution of means between the measures of reducing anthropogenic dumping on the one hand, and measures on maintaining, or even increasing, the self-cleaning potential of the marine water areas on the other.

Secondly, the realization that the proposed approach brings about necessary premises for preventive accomplishment of nature protection programs. This circumstance is very important because no other part of the biosphere is in such a need of preventive protection as the marine and oceanic environment. The enormous inertia of the world's oceans makes possible a long-term and concealed accumulation of polluting components and anthropogenic disturbances. By the time the undesirable consequences of these disturbances are authentically documented and impose their harmful effect the marine environment, and the branches of economy connected with it, their elimination will be a long-time procedure requiring large-scale and exceptionally complicated organizational and economic efforts of society. It may also be stated, _a priori_, that the required expenditure, in this respect, will be much greater than the cost of preventive maintenance programs.

The above-mentioned principal approach to controlling the economic-ecological system, with reference to the protection of the marine environment from pollution, assumes, first of all, the determination of the MPD as a controlling criterion.

In a general way, the procedure of searching for the MPD includes finding the dependence of the concentration of pollutants, (C), as a function of space, (R), and time, (t), on the amount of dumping, (Q), the intensity of its dispersion as a result of turbulent diffusion, adsorption, sedimentation, etc. ($\lambda_1, \lambda_2 \ldots \lambda_n$), as well as the rate of self-cleaning, (S), of the environment, i.e.:

$$C = C\ (Q, S, \lambda_1, \lambda_2\ \ldots \lambda_n,\ \overline{R},\ t) \qquad (1)$$

Using the values of MPC as predetermined limits for the concentration of pollutants (condition: $C \leq$ MPC), we derive the following inequality:

$$C = (Q, S, \lambda_1, \lambda_2\ \ldots \lambda_n,\ \overline{R},\ t) \leq MPC \qquad (2)$$

which is fulfilled at $Q \leq$ MPD, where MPD is determined from the relation:

$$C\ (MPD,\ S, \lambda_1, \lambda_2 \ldots \lambda_n,\ \overline{R},\ t) = MPC \qquad (3)$$

It is of great importance that for any fixed point in the water area, the maximum permissible dumping is limited by the self-cleaning capability of the surrounding environment. In this connection, with the aim of making utmost use of environmental capabilities, the value of MPD should be set under the condition that S = SCP, so that the values of MPD, MPC, and SCP are linked through the following relation:

$$C(MPD,\ SCP, \lambda_1, \lambda_2 \ldots \lambda_n,\ R,\ t) = MPC \qquad (4)$$

It should be noted that in spite of the apparent simplicity of the proposed formalized pattern of determining the MPD, a number of complicated problems which must be solved arise when studying the pattern in detail. The main problems can be shown by the following example illustrating the determination of the maximum permissible dumping with the following assumptions:

1) A function $q = q(Q, \lambda_1, \lambda_2 \ldots \lambda_n,\ \overline{R})$ is given, where (q) is the rate of concentration change of the pollutants determined at the given point of the water area by the dumping, (Q), and further dispersion (turbulent diffusion, adsorption, sedimentation);

2) The function of the self-cleaning rate is known, which depends only on the concentration of the pollutants. This function is shown hypothetically in Fig. 1.

In this case the dynamics of concentration may be presented by the following differential equation:

$$\frac{dC}{dt} = q(Q, \lambda_1, \lambda_2 \ldots \lambda_n,\ \overline{R}) - S(C) \qquad (5)$$

With initial conditions of $t=0$, $C=C$. (6)

The equation (5) with conditions (6) is solved as:

$$\int \frac{dC}{q-S(C)} + K(Co) = t,$$

where $K(C_o)$ is a constant of integration.

To investigate the solution obtained, let us assume that the dumping rate is a constant value (q=const), and the relation, $S(C)$, at its maximum, is approximated by the function shown in Fig. 1 by a dotted line and presented as:

$$S(C)=\frac{S^*}{C^{*2}} C(2C^*-C),$$

where S^* and C^* are coordinates of the self-cleaning function maximum, or in other words, self-cleaning potential.

In this case the solution can be written as:

$$\int \frac{dC}{q - \frac{S^*}{C^{*2}} C(2C^*-C)} + K(C_o) = t$$

Passing to dimensionless variables $\alpha = \frac{C}{C}$, and $\tau = \frac{t}{C^*S^*}$ and introducing a dimensionless parameter $\lambda = \frac{g}{S}$, we get:

$$\int \frac{d\alpha}{(\lambda-1) - (\alpha-1)} + K(\alpha_o) = \tau \qquad (7)$$

The solutions obtained as a result of integration (7) depend on the value of λ and are written as:

$$\text{At } \lambda > 1 \ \alpha = \frac{\alpha_o\sqrt{1-\lambda}-(\alpha_o-\lambda)t\lambda(\tau\sqrt{1-\lambda})}{\sqrt{1-\lambda}-(\alpha_o-1)t\lambda(\tau\sqrt{1-\lambda})}; \qquad (8)$$

$$\text{At } \lambda = 1 \ \alpha = \frac{\tau(1-\alpha_o)+\alpha o}{1+\alpha(1-\alpha_o)} \ ; \qquad (9)$$

$$\text{At } \lambda < 1 \ \alpha = \frac{\alpha_o(1+\sqrt{1-\lambda})-\lambda+ \lambda-\alpha o(1-\sqrt{1-\lambda}) \ e^{2\tau\sqrt{1-\lambda}}}{-\lambda +\alpha_o-1-(\alpha_o-1-\sqrt{1-\lambda})e^{\alpha\tau\sqrt{1-\lambda}}} \qquad (10)$$

The equation (8) confirms the self-evident conclusion that at $g> 1$, i.e. under conditions when the amount of dumping at the given point of the water area exceeds the self-cleaning potential, irrespective of the initial concentration $C_o(\alpha_o < 1, \alpha_o > 1)$, there is always such an interval of time $= \frac{1}{\sqrt{\lambda-1}}$ arctg $\left(\frac{\sqrt{\lambda-1}}{\alpha_o-1}\right)$ at which the concentration of the pollutants becomes impermissibly high (Fig. 2a).

From the above follows an important principal point, according to which the value of MPD for excessively polluted water areas should be set at a substantially lower level than the environmental self-cleaning potential.

At $\lambda < 1$ (Fig. 2c), depending on the initial concentration of the pollutants, the solving of the equation (5) under initial conditions (6) is always stable, but it may tend to two different limits:

$$\alpha' = \lim_{\tau \to \infty} \alpha = 1-\sqrt{1-\lambda} \quad \text{and} \qquad (11)$$

$$\alpha'' = \lim_{\tau \to \infty} \alpha = 1+\sqrt{1-\lambda}$$

Passing from dimensionless variables to concentrations, we can write (11) as:

$$C' = C^*(1-\sqrt{1-\lambda}) \quad \text{and}$$

$$C'' = C^*(1+\sqrt{1-\lambda})$$

As seen from Fig. 2c at $C_0 < C''$ ($\alpha_0 < \alpha''$) the concentration of pollutants in the water area will tend to C'. Thereby, if the initial concentration exceeds $C^*(\alpha_0 > 1)$, then up to a certain moment τ the content of pollutants in the water area is practically stable. Such an unfavorable situation, however, is temporary, and it reflects the inertia of the self-cleaning process. It does not, however, signify that the relation between MPD and SCP is unfavorable. The objective evaluation in this case demands investigation and establishment of real values of the parameter λ.

At $C_0 > C''(\alpha_0 \geq \alpha'')$ the concentration of pollutants in the water area decreases monotonically, approaching the value C", at which the addition content is rather high and exceeds the concentration C* corresponding to the environmental self-cleaning potential.

As the maximum (potential) of self-cleaning is attained at a certain concentration, (C*), when setting up the MPD as a control criterion, it will be necessary to also consider the value of the relation between MPC and C*. The characteristic matrix of the possible situations arising at various values of λ, as well as various relations of C_0/C^*, and MPC/C^*, is shown in Fig. 1.

The data shown allow a number of problems to be basically solved. These problems are important to the selection of the strategy for the qualitative control of the marine environment.

As seen from Table 1, under conditions of an actual situation, i.e. at MPC < C*, the desirable result of control, maintaining the content of pollutants at a level lesser or equal to the MPC, may be obtained only when $\lambda < 1$ (conditions 1.4, and 1.5, Table 1).

At MPC > C* this result is obtained both at $\lambda = 1$ (conditions 2.1, 2.2, 3.1, 3.2), and at $\lambda < 1$ (conditions 2.3, 3.4, 3.5). In this case, naturally, a

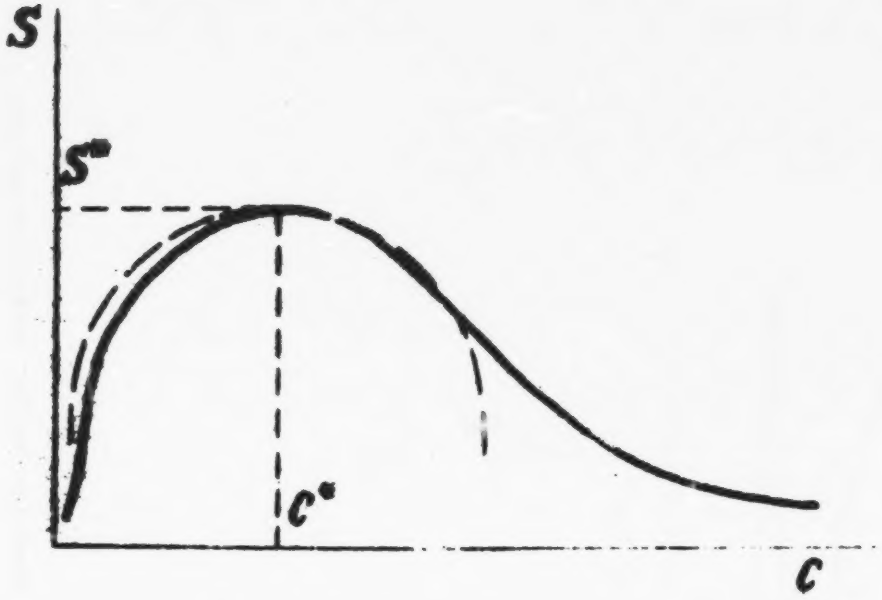


Figure 1. Hypothetical form of relationship between rate of self-cleaning and concentration.

Of particular interest are situations at which $\lambda = 1$ and $\lambda < 1$. In the first case, when the intensity of dumping is close to the self-cleaning potential of the marine environment, the dynamics of the concentration change are determined entirely by the initial pollution of the water area (Fig. 2b). If $C_0 \leq C^*(\alpha \leq 1)$, then the content of pollutants in the water basin rises monotonically, approaching $C^*(\alpha = 1)$ asymptotically. At $C_0 > C^*(\alpha > 1)$, it grows similar to the case, λ 1.

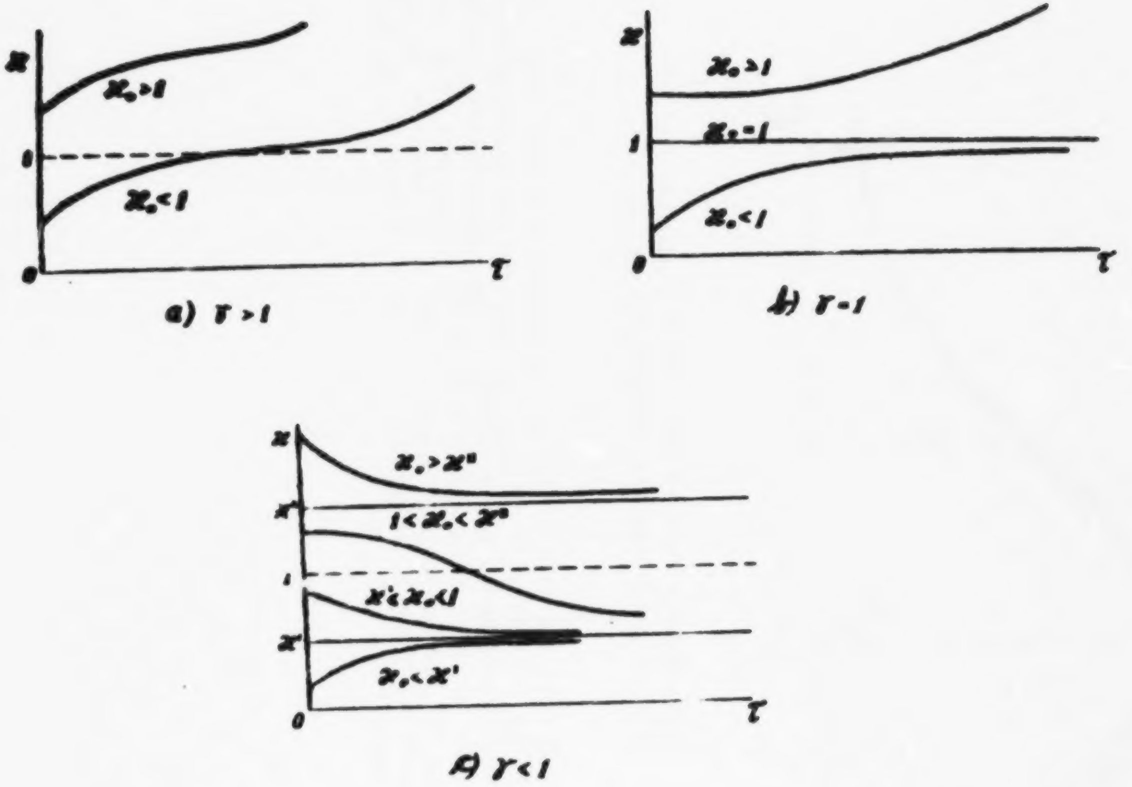


Figure 2. Change of dimensionless variable $\varkappa = C/C^*$ with time depending on its initial values and value of dimensionless parameter λ.

number of control alternatives arise which are unequal to the expenditure they require for their fulfilment. It is especially evident that the expenditure, being a decreasing function of the MPD, is considerably greater when $\lambda=1$, than when $\lambda<1$.

TABLE 1

		Increase of concentration of pollutants corresponds to marine environment self-cleaning potential, $\lambda=1$			Increase of concentration of pollutants less than marine environment self-cleaning potential, $\lambda<1$	
		$C_0 < C^*$ 1	$C_0 = C^*$ 2	$C_0 > C^*$ 3	$C_0 < C^*$ 4	$C_0 > C^*$ 5
$MPC < C^*$	1	MPC will be exceeded in a certain period of time	MPC cannot be reached	MPC cannot be reached	MPC maintained at all times	MPC reached in a certain period of time
$MPC = C^*$	2	MPC maintained at all times	MPC maintained at all times	MPC cannot be reached	MPC maintained at all times	MPC reached in a certain period of time
$MPC > C^*$	3	MPC maintained at all times	MPC maintained at all times	MPC will be exceeded in a certain period of time	MPC maintained at all times	MPC maintained at all times

It may be noted that at $\lambda=1$ the values of MPD and SCP are equal, and at $\lambda<1$ the interrelation of the investigated criteria following from the equation (11) may be written as:

$$MPD=SCP\ [1-(1-\frac{MPC}{C+})^2] \qquad (12)$$

Actually the above-mentioned control alternatives are more numerous. As within the conception of controlling the economic-ecological systems, there is a basic possibility of varying the value of λ, not only by varying the maximum permissible dumpings, but also by the potential ability of the marine environment for self-cleaning. By this, it is meant that the value of the self-cleaning potential can be increased by the adjustment of such environmental parameters as salinity (5), content of biogenic elements, introduction of special bacteria-destruction strains, increasing the relative share of filtrating organisms in the ecological system, etc. Thereby, under the condition of λ=MPD/SCP-const, owing to the increase of the environmental self-cleaning potential, the possibility arises of increasing the MPD and, accordingly, reducing the costs for its attainment and maintenance. In this case, naturally, a number of control alternatives arise, including the possibility of choosing an optimum method according to the minimum total expenditure criterion. The practical solution of this problem is of particular interest and should be the subject of an independent investigation.

The foregoing indicates that, for the qualitative control of the marine environment, it will be necessary to extend information units of chemical pollution monitoring by introducing into the system some defining factors of a number of parameters, such as:

- quantity and composition of anthropogenic wastes dumped into the sea from local polluting sources;

- a set of parameters allowing an estimate of the processes of dispersion of pollutants as a result of turbulent diffusion, adsorption, and sedimentation;

- concentration of pollutants, (C^*), corresponding to the maximum of the environmental self-cleaning ability (S^*).

A distinct position is thereby taken by the experimental determination of the form of the function $S(C)$ for the water areas investigated, or separate chambers characteristic of them.

The solving of the latter problem is possible in two ways. The first way consists of a detailed study of all the defining factors with subsequent development of simulated models of the process. The second, and a more acceptable, way is to select a system of integrating indices allowing a macro-description of the function being sought. Substantiating the system of these indices is a separate task which is beyond the scope of this report. However, some problems to be proposed are the energy of activation and the constant of the dissociation rate of pollutants, which are rather easily determined by experiment.

It is evident that within the scope of a single paper it is impossible to explain all the points of such a complicated problem as the qualitative control of the marine environment. The interpretations set forth in the foregoing lines consisted only of shaping the principal aim of control, proving the basic possibilities, and determining the ways of attainment of control in practice. The final stage, completing this work, seems to be the elaboration of a system for economic-ecological planning and control.

The proposed schematic diagram (Fig. 3) allows us, firstly, to trace the place of monitoring and, second, to determine the whole complex of requirements imposed upon this control on the part of the system as a whole, and, finally, to show the relationship between the information flows within the system.

As seen from Fig. 3, the functional scheme of economic-ecological control is proposed to be built in the form of four units: monitoring, (1); ecological, (2); and economic, (3); predicting, and economic-ecological planning proper, (4).

The object of control, contemplated as a unified economic-ecological system, is represented in the diagram in the form of two units: "economy", (5); and "environment", (6). Considering the nature of links between them it seems feasible to organize monitoring comprising three kinds of observations

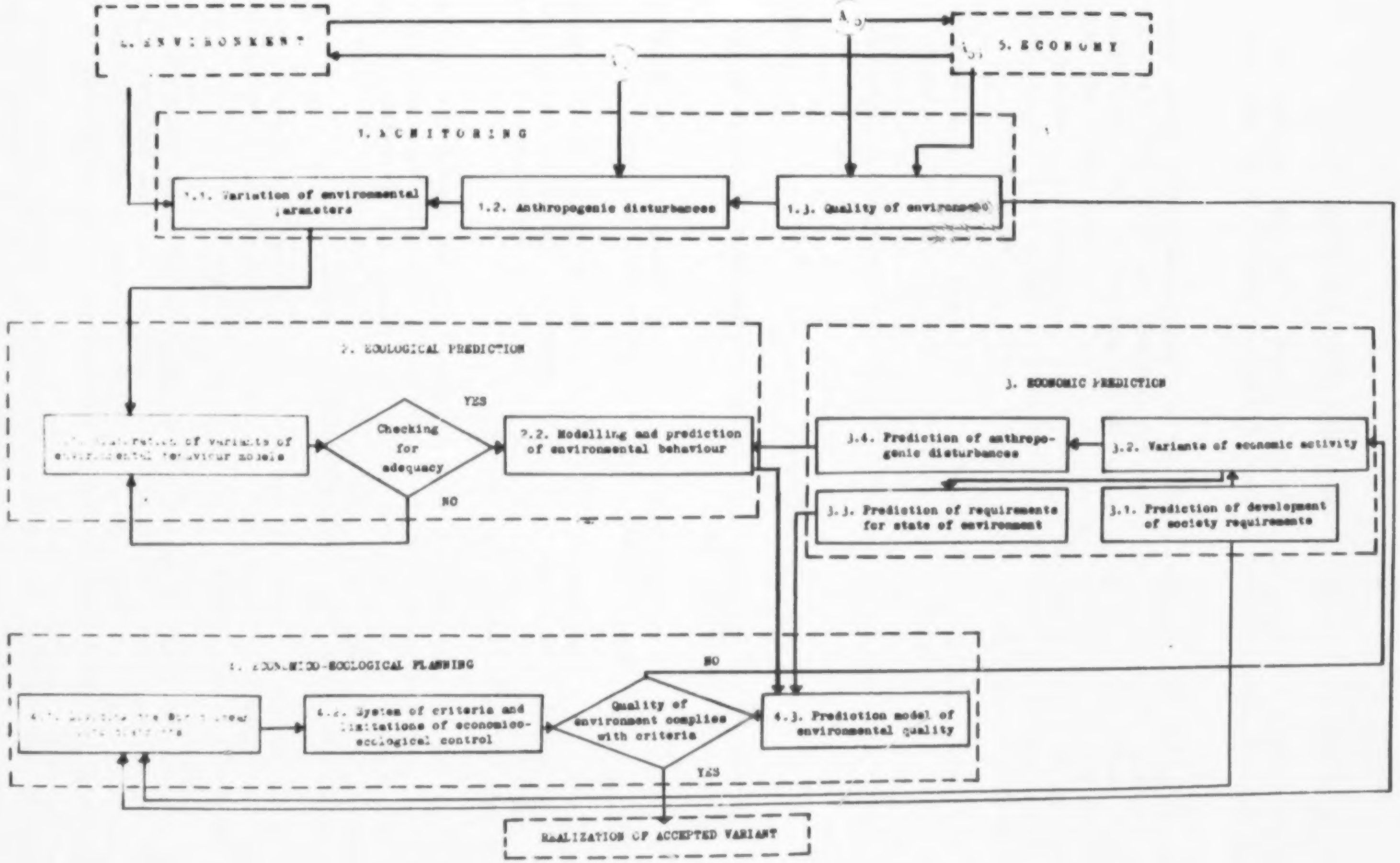

6. ENVIRONMENT
5. ECONOMY
1. MONITORING
1.1. Variation of environmental parameters
1.2. Anthropogenic disturbances
1.3. Quality of environment
2. ECOLOGICAL PREDICTION
2.1. [illegible] of variants of environmental behaviour models
Checking for adequacy
YES
NO
2.2. Modelling and prediction of environmental behaviour
3. ECONOMIC PREDICTION
3.4. Prediction of anthropogenic disturbances
3.2. Variants of economic activity
3.3. Prediction of requirements for state of environment
3.1. Prediction of development of society requirements
4. ECONOMICO-ECOLOGICAL PLANNING
4.2. System of criteria and limitations of economico-ecological control
Quality of environment complies with criteria
NO
YES
4.3. Prediction model of environmental quality
REALIZATION OF ACCEPTED VARIANT

Figure 3. Schematic diagram of economic-ecological planning system.

necessary for controlling purposes, viz.:

A_{56} - concerning the nature of anthropogenic disturbances;

A_{65} - concerning the physical, chemical, and biological parameters of the state of environment included in the production function of consumer goods.

If, for denoting the routine state of the environment the above information is sufficient, the predicting purposes require the knowledge of the transformation mechanism of anthropogenic disturbances in the environment. The information basis for modelling, and prediction in this case, may serve the knowledge of the variations of the environmental parameters both as a result of anthropogenic activity and the climatic conditions. It is this kind of information, denoted as A_{66}, that is shown on the diagram.

Under the requirements of information on the part of the observation system, A_{65}, this information is necessary for the determination of the dependence of industrial activity effectiveness on the state of the environment. This dependence can be written in the form of production functions as follows:

$$P = f(F_1, F_2 \ldots F_K)\, \psi(\alpha_1, \alpha_2 \ldots \alpha n) \qquad (14)$$

where: P is the result of the operation of an enterprise (finished product, production costs, effectiveness, etc.);

$f(F_1, F_2 \ldots K_k)$ is a function describing the dependence of the results on the economic factors (basic funds, labor expenditure, etc.);

$\psi(\alpha_1, \alpha_2 \ldots \alpha n)$ is a function of influence of the state of the environment determined unequivocally as a set of physico-chemical, dynamic, biological, and similar parameters, $\{\alpha i\}$ (salinity, temperature, concentration of adequate ingredients, dynamics of flows, streams, etc.).

Monitoring the marine environment determines the values of the ecological parameters $\{\alpha i\}$. At the same time, for plotting production functions such as, (14), special information is required as to the values and dynamics of the economic factors $(P, F_1, F_2 \ldots F_k)$. This involves the necessity to also supplement monitoring with the observation system A_{55}.

Thus, it is proposed to single out four basic systems to observe the state of the environment and economic activity, having unified them by the concept of economic-ecological monitoring (subsystem 1, Fig. 3).

As may be seen from the diagram, the economic-ecological monitoring includes the following functional units: 1.1 and 1.2 are the information processing systems A_{56}, and A_{66}, for clarifying the functional relations between the state parameters subjected to anthropogenic disturbances.

1.3 are the information processing systems A_{55}, and A_{65}, for determining the quality of the environment, i.e. evaluation of its state, accomplished by the respective consumer.

If the content of units 1.1 and 1.2 is sufficiently evident, the concept of the equality of the environment requires some clarification. Actually, the quality of the environment is an economic evaluation of the compliance of its state with the requirements of the respective consumer. Thus, a certain state of the environment may be satisfactory for one consumer, and unsatisfactory for another.

When considering the requirements of society in all its diversity, it may be feasible to single out three types of marine water areas: protected zones, health resort zones, and regions of high economic use. Accordingly, the concept of quality of the marine environment is different for these types of water areas. In the first case, the quality of the environment is evaluated by the degree of the state of preservation of the ecological systems. In the second case, the quality is determined by the degree of compliance with the social and hygienic requirements. And, finally, in the third case, the economic evaluation of the environmental quality may be defined by comparing the current effectiveness of its use with the maximum possible effectiveness. The subject of this investigation, in our view, may be the production functions as in (14).

In the ecological prediction subsystem (2), various environmental behavior models (unit 2.1) are shaped according to the information (1.1), the adequacy of which being checked by means of the retrospective and current data on the strength of the information 1.1 and 1.2. The final functioning result of the subsystem (2) is the elaboration of the environmental system of models (2.2), allowing the dynamic of the basic parameters of the state of the environment to be predicted. In supplement to the problems connected with the pollution of the marine environment, this unit includes, as a minimum, the modelling of the processes of disperson of pollutants, self-cleaning, etc., with their subsequent unification into a common concentration dynamic model, similar to that described by the equation (5).

In the economic prediction subsystem, (3), variants of economic activity, (3.3), are elaborated on the basis of the development of requirements, (3.2), providing for their statisfaction.

The specific feature in operating the economic-ecological systems is that the interaction of the "economy" and "environment" takes place at a level of separate enterprises in specific regions. Consequently, the operation of this unit is accomplished at two levels: macroeconomic and microeconomic, the latter comprising production functions.

On the basis of the production functions for each of the variants, certain requirements for the parameters of the environmental state are formed. The list of these parameters should be included in any monitoring program concerning the observation system A_{65}.

Information on the extent and nature of the anthropogenic disturbances, deposited with the unit, 3.4, is determined by considering the technology and the volume of output (defined by the respective variants of economic activity).

The information worked out by the unit, 3.4, is employed in the environmental modelling (unit 2.2). In its turn, the information of unit 3.3, in conjunction with the prediction of the environmental state (output of unit 2.2), is the basis for modelling the quality of the environment (which takes place in unit 4.3).

In the subsystem 4, the conjugation of the variants of economic activity with the predicted state of the environment is accomplished, i.e. the economic-ecological planning proper. For this purpose, provision is made for a unit, (4.2), in which various criteria and limitations of the water areas with different characters of employment are worked out. The division into districts, required for this purpose, is performed in unit 4.1, on the basis of the information data on the current state and quality of the marine environment, (unit 1.3), and the society requirement prediction (unit 3.1) with respect to the contemplated character of utilizing the water areas.

The problem of choosing the criteria of economic-ecological control is a complicated and independent task. Solution of this problem is not connected with the problems of monitoring of the marine environment. Establishment of scientifically founded limitations is, as follows from the foregoing lines, one of the main functions of chemical pollution monitoring. Returning to Table 1, we want to recall that the establishment of the MPC and MPD as limitations of economic-ecological control is determined, principally, by the value of the self-cleaning potential (SCP), and also by the values of C_O, C^*, and finally, by the relation between MPC and C^*.

In this way, requirements of economic-ecological control, with the aim of protecting the marine environment from pollution, sets up a monitoring problem to determine the fields of C_O, C^* and SCP for various water areas of the world's oceans. Solving this problem will permit their division into districts and subsequent forming of a differential strategy to permit balanced development of regional economic-ecological systems.

Only by applying the described approach to control of these systems of ever-growing scale can chemical pollution of the marine environment be prevented.

It is quite evident that the statements put forth in this work lay no claim to being complete, but are only contemplations for more important problems which should be solved within the scope of protecting the sea resources from their quantitative and qualitative exhaustion. Many of the points are described in the form of problems, and their discussion, development, and realization are contemplated by us as very perspective tasks.

REFERENCES

1. Meleshkin, M.T. 1975. Fundamentals of Programmed Planning of Economic Exploitation of the World Ocean. In: Problems of Sea Economy, is.4, Odessa.

2. Meleshkin, M.T, and A.L. Suvorovskiy, et al. 1974. Methodological Fundamentals of the World Ocean Economy. Vestnik No. 12, Ac.Sci.USSR.

3. Ananitchev, K.V. 1974. Problems of Environment, Energy and Natural Resources, Moscow, Progress.

4. Izrael, Uy.A. 1975. Complex Analysis of Environment. Approaches to Determining Permissible Loads on Environment and Substantiation of Monitoring. In: Comprehensive Analysis of the Environment, Gidrometizdat, Leningrad.

5. Bronfman, A.M. 1976. Alternative Solving of Economic-Ecological Problems in the Azov Sea Basin. In: Problems of Sea Economy is. 5, Odessa.

APPENDIX

PROTOCOL OF THE WORKING MEETING OF SOVIET AND AMERICAN SPECIALISTS ON THE RESULTS OF THE SOVIET-AMERICAN INTERCALIBRATION OF METHODS OF DETERMINING OIL AND OIL PRODUCTS IN SEAWATER DURING AN EXPEDITION AT SEA

Odessa. May 24, 1977

After discussing the results of the intercalibration of methods for determining oil and oil products in seawater during the voyage of the research vessel Musson in the Atlantic Ocean (December 1975 to January 1976), the participants note that:

1. Standard solutions exchanged and analyzed by using the infrared method show nearly identical results.

2. The infrared red absorbtion at 2930 cm^{-1} of the CCL_4 used by the American and Soviet sides prove also to be nearly identical.

3. The data on oil concentrations in some extracts made during the cruise with an OIL 102 Yanagimoto Oil Analyser are similar to results obtained for unprocessed samples in land-based laboratories in the U.S. and U.S.S.R.

4. Some discrepancies in the analysis of processed samples were probably caused during individual stages of analyses (sampling methods, extraction, vacuum concentration, drying of the extract, or column chromotography). In addition, the seawater divided on board into two parts may have been in homogenous in oil concentration. These variables cannot be controlled at sea.

5. Both sides think that it is advisable to carry out the second stage of intercalibration of methods for determining oils and oil products under laboratory conditions. During this stage, both sides will compare all sampling procedures. Prior to the laboratory intercalibration, it is necessary to complete a detailed program for this work.

Both sides will exchange draft programs before October 1977. The program should be finalized and exchanged under the auspices of the Joint U.S.-U.S.S.R. Committee on Cooperation in the Field of Environmental Protection by January 1978. Both sides propose that this laboratory work will be carried out in the U.S. during the second half of 1978.

6. A joint report of the results of oceanic samples and laboratory intercalibration will be made after completion of the laboratory work.

7. Data from the joint cruise will be kept in the individual laboratories in the U.S. and the U.S.S.R.

U.S. Side
Dr. T. Duke T. Duke
Dr. R. Hittinger R. Hittinger

U.S.S.R. Side
Dr. A. Simonov
Dr. S. Oradovski